CALIBRATION OF THE PCB WATER QUALITY MODEL FOR THE DELAWARE ESTUARY FOR PENTA-PCBs AND CARBON

Delaware River Basin Commission

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The approach to calibration of the PCB TMDL model for the Delaware River and Estuary was developed by Victor J. Bierman, Jr. and Scott C. Hinz of Limno-Tech, Inc. at the request of the Delaware River Basin Commission (DRBC). This approach was consistent with the recommendations of the Expert Panel convened by DRBC to provide independent scientific review of the overall modeling effort. Dr. Bierman and Mr. Hinz wrote the Model Calibration Approach section of the Model Calibration Report.

The decadal scale consistency check was performed by Ferdi L. Hellweger and Dominic M. Di Toro of HydroQual at the request of the DRBC based upon the recommendation of DRBC's Expert Panel. Funding for HydroQual's decadal scale consistency check was provided by the Delaware Estuary TMDL Coalition. Mr. Hellweger and Dr. DiToro wrote the Decadal Scale Consistency Check section of the Model Calibration Report.

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EXECUTIVE SUMMARY

The overall objective of the model calibration was to accurately represent the principal environmental processes influencing the transport and fate of penta-PCBs in the Delaware River and Estuary. These processes include hydrodynamics, sorbent (organic carbon) dynamics and partitioning of PCBs to organic carbon in the water column and bedded sediments. This model was calibrated to ambient data for biotic carbon (BIC) and particulate detrital carbon (PDC) in the water column, and to available data for net solids burial in the sediments. Finally, the calibrated sorbent dynamics model was used to drive a mass balance model of penta-PCBs in the water column and sediments.

Daily loads of organic carbon and penta-PCB were estimated for each day of the 577 day continuous simulation period spanning September 1, 2001 through March 31, 2003 for relevant source categories, including contaminated sites, non-point sources, point discharges, model boundaries, tributaries, atmospheric deposition, and CSOs. In order to assess the uncertainty associated with the load estimation calculations, a Monte Carlo analysis was performed for each of the PCB source categories. This analysis allowed estimation of the uncertainty for each source category, comparisons of uncertainty between categories, and identification of reasonable upper and lower limits for loadings for each category and for the overall penta-PCB load. Scaled loads corresponding to the 20^{th} and 80^{th} percentile of the overall penta-PCB loading range yielded water column concentrations within -10% to +20% of the unscaled loads.

Ambient water samples were collected from the mainstem Delaware Estuary for the analysis of particulate and dissolved PCBs, total suspended solids, and particulate and dissolved organic carbon. Twenty four main stem channel sites were sampled under a range of flows. The data collected allowed initial quantitation of dissolved and particulate PCB levels as well as organic carbon in the mainstem Delaware Estuary. The resultant monitoring data were used as calibration targets for the model.

DRBC and LTI enhanced EPA's Water Quality Simulation Program (WASP) Version 5.12 to develop a general purpose sorbent dynamic PCB model for the Delaware River Estuary. The model simulates tidal flows, and spatial and temporal distributions of organic carbon (OC) and penta-PCB. Comparisons of simulated to measured water quality concentrations indicate generally good agreement and low bias of the estimate for organic carbon and penta-PCB. The correlation coefficients for particulate and dissolved penta-PCB exceed EPA's recommended correlation coefficient acceptance criteria for water quality variables.

Historical hindcast simulations (1930-2002) were performed to check the long-term (decadal scale) behavior of the model. A review of the hindcast simulation results using the current model showed: (1) The model is in reasonable agreement with the historical water column concentrations, both observed and deduced from the dated core for the period following the 1980s; (2) The model is in reasonable agreement with the contemporary sediment data in the upper estuary (Zones 2-3); (3) The model appears to be inconsistent with the historical sediment data; (4) The model predicted time course of water column and sediment bed concentrations also appear to be inconsistent with the fish tissue concentrations. At present it is not clear what the source(s) of the two inconsistencies (sediment and fish tissue) is (are). Possible causes include error(s) in (1) forcing functions (current and/or historical), (2) the model (e.g. mixed layer depth) and/or (3) the data or how they are interpreted.

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1 Model Calibration Approach

The overall objective of the model calibration was to accurately represent the principal environmental processes influencing the transport and fate of penta-PCBs in the Delaware River and Estuary. These processes include hydrodynamics, sorbent (organic carbon) dynamics and partitioning of PCBs to organic carbon in the water column and bedded sediments. The first step in the process was calibration of the hydrodynamic model to available data for tidal heights and confirmation of this calibration by using the computed hydrodynamics to drive a mass balance model for salinity (chloride). The calibrated hydrodynamic and salinity model was then used as a "hydraulic chassis" to drive a mass balance model of organic carbon sorbent dynamics. This model was calibrated to ambient data for biotic carbon (BIC) and particulate detrital carbon (PDC) in the water column, and to available data for net solids burial in the sediments. Finally, the calibrated sorbent dynamics model was used to drive a mass balance model of penta-PCBs in the water column and sediments.

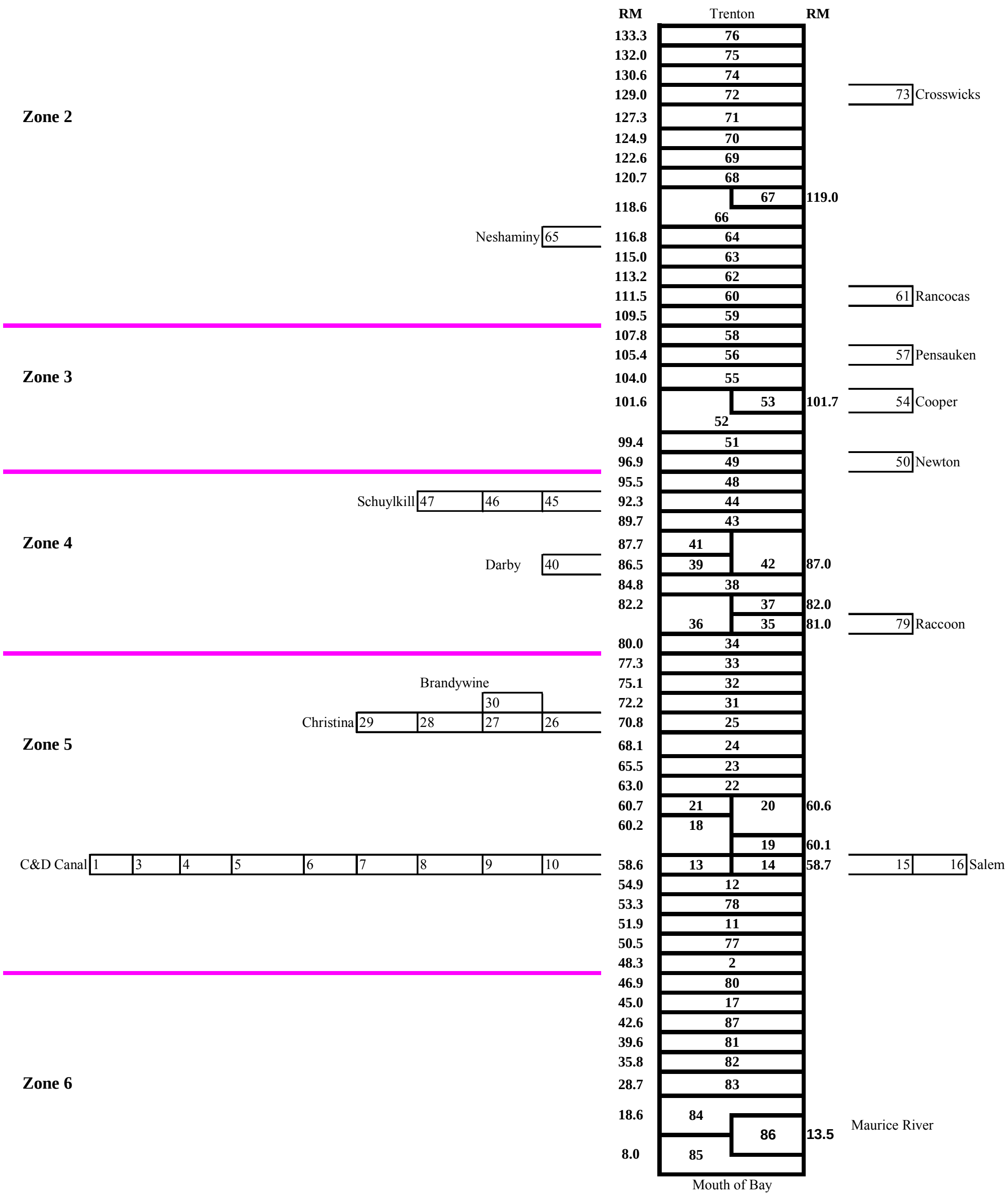
The hydrodynamic, sorbent dynamics and penta-PCB models were calibrated to available data for the period from September 2001 through March 2003. This period contained the most comprehensive data for salinity, organic carbon and penta-PCBs for the Delaware River and Estuary. Continuous dynamic simulations were conducted with all three of the coupled mass balance models for this 19-month period. For a hydrophobic organic chemical (HOC) like PCBs, this approach is necessary but not sufficient to constrain all of the controlling environmental processes. In particular, water column PCB concentrations in rivers or estuaries typically respond to changes in external loadings or sorbent dynamics on time scales of days to weeks. In contrast, sediment PCB concentrations typically respond on time scales of years to decades because PCBs are much less mobile in bedded sediments. Consequently, if sediment-water interactions are important in controlling the overall response of PCBs in a system, these dynamics can only be calibrated using decadal-scale simulations and long-term historical data.

A major obstacle to conducting a rigorous decadal-scale PCB model calibration for the Delaware River and Estuary is that historical data for PCB loadings and responses are extremely limited. Nonetheless, given the importance of exercising the penta-PCB model to assess its long-term performance, a decision was made to conduct a decadal-scale consistency check on the short-term 19-month calibration. This check involved conducting a 74-year hindcast simulation for penta-PCBs from 1930 through 2003. Because reconstruction of historical penta-PCB loadings required many assumptions, emphasis was placed only on broad trends and temporal structure of the hindcast simulation results, not on absolute comparisons to historical data. Results from these simulations were used to inform decisions on sediment-water cycling rates and surface sediment layer mixed depths in the short-term 19-month calibration. These are the principal model parameters that control sediment-water PCB interactions and hence the long-term behavior of the penta-PCB model.

Figure 1.1 shows a map of the Delaware Estuary, including the Water Quality Management Zones. Figure 1.2 shows the model segmentation for the PCB TMDL water quality model.

Figure 1.1 - Map of the Delaware Estuary Including Zones

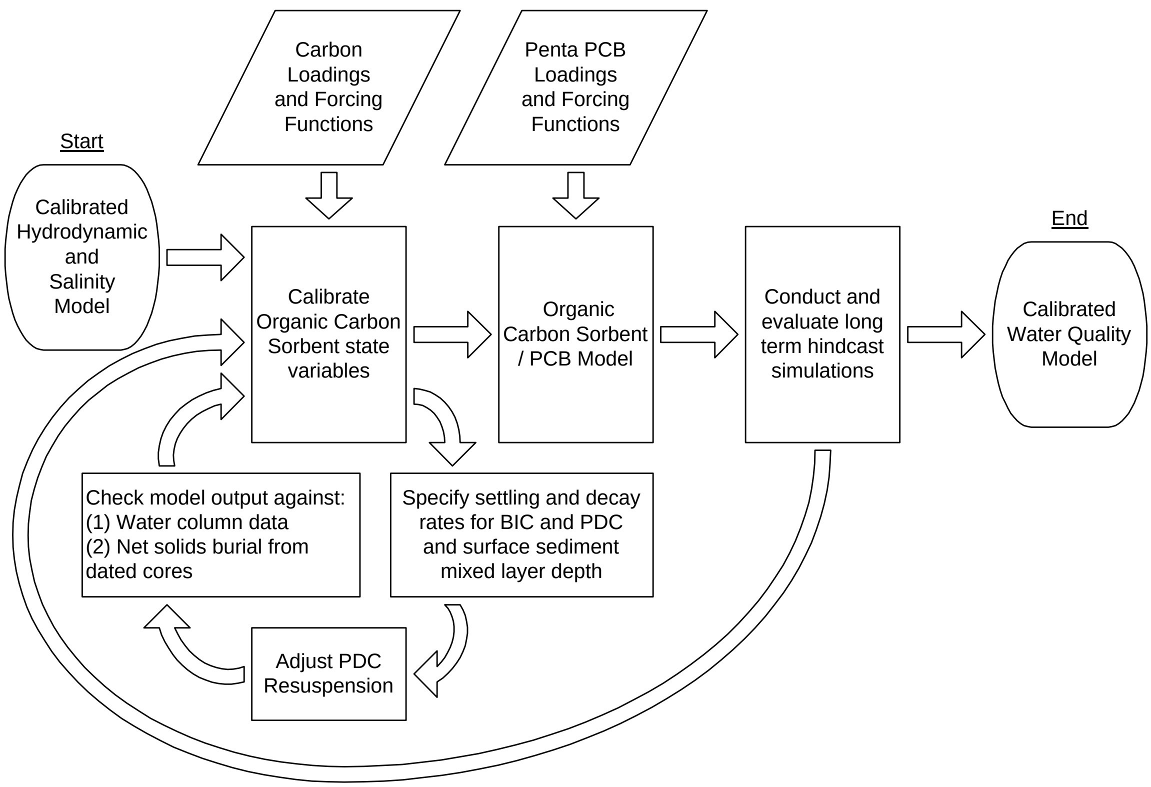
Figure 1.2 - Schematic Diagram of the PCB TMDL Water Quality Model



1.2 Model Calibration Strategy

The general calibration strategy was to specify as many external inputs and internal model parameters as possible using site-specific data or independent measurements, and only a minimal number of parameters through model calibration. Another part of the strategy was that parameters determined through model calibration were held spatially and temporally constant unless there was supporting information to the contrary. Model parameters were not permitted to assume arbitrary values in order to obtain the best "curve fits" in a strictly mathematical sense. Emphasis was placed on best professional judgment and on results from a suite of different metrics that were used collectively in a weight-of-evidence approach. Figure 1.3 shows a simplified schematic representation of the model calibration approach.

Figure 1.3 - Model Calibration Approach



1.2.2 Organic Carbon Sorbents

The calibrated hydrodynamic and salinity model was used as a "hydraulic chassis" to drive the organic carbon sorbent dynamics model. The hydrodynamic and salinity calibrations are described in a previous section of this report. The following were the principal steps in calibration of the organic carbon sorbent dynamics:

- Specify a constant net settling rate for BIC.
- Specify a constant gross settling rate for PDC.
- Specify temperature-dependent PDC and BIC decay rates in the water column.
- Specify a temperature-dependent PDC decay rate in the sediment consistent with available data for sediment oxygen demand.
- Adjust PDC resuspension rates for each spatial zone or sub-zone to achieve optimal agreement between model results and available data for water column PDC concentrations and net solids burial rates.
- Conduct sensitivity analyses on model parameters over ranges consistent with the scientific literature, other modeling studies and best professional judgment to obtain optimal agreement between computed and observed values.
- Adjust PDC gross settling and resuspension rates, and surface sediment layer mixed depths, to achieve consistency between results from the short-term 19-month calibration and the 74-year hindcast simulations.

1.2.3 penta-PCBs

The calibrated organic carbon sorbent dynamics model was used to drive the mass balance model of penta-PCBs in the water column and sediments. All external inputs and internal model parameters for penta-PCB were specified using site-specific data or independent measurements. No penta-PCB model parameters were determined through model calibration. Furthermore, there was only feed-forward from the short-term organic carbon sorbents calibration, not feed-back from the short-term penta-PCB calibration. That is, results from the short-term penta-PCB simulations were not used to retroactively adjust any of the model parameters in the short-term organic carbon sorbents calibration.

There was feed-back from the 74-year hindcast simulations to the short-term organic carbon sorbents calibration. Results from the 74-year hindcast simulations were used to inform final decisions on sediment-water cycling rates and surface sediment layer mixed depths in the short-term calibration. Sediment-water cycling rates for penta-PCBs are determined primarily by the magnitudes of PDC gross settling and resuspension velocities in the model. Surface sediment layer mixed depths are controlled by the mixing rate between the top two surficial sediment layers in the model. These model parameters can not be fully constrained during a short-term calibration period, but can only be calibrated using decadal-scale simulations and long-term historical data.

1.3 Model Calibration Metrics

To inform decisions on model parameters that were determined through calibration, a suite of different metrics was used to compare model output with available data. These metrics included both graphical and statistical methods. Results of load uncertainty analyses, discussed in Section 2.7, were also used considered. Two different sets of metrics were used, one set for the short-term calibration and another set for the decadal-scale simulations. Results from the different metrics were used collectively in a weight-of-evidence approach and all final calibration decisions were based on best professional judgment.

1.3.1 Short-Term Calibration

The following were the principal metrics used for the short-term, 19-month model calibration:

- Longitudinal plots of computed and observed annual net solids burial rates.
- Longitudinal plots of computed and observed water column concentrations for PDC, BIC and penta-PCB concentrations (total, particulate, dissolved and normalized to particulate organic carbon) at fixed points in time.
- Cumulative frequency distributions for matched pairs of computed and observed values for PDC, BIC and penta-PCB concentrations.
- Time series plots of computed and observed PDC, BIC and penta-PCB concentrations for each spatial zone.
- Bivariate plots of computed and observed values for PDC, BIC and penta-PCB concentrations.

1.3.2 Decadal-Scale Consistency Check

The following were the principal metrics used for the 74-year hindcast simulations:

- Time series plots of computed (estimated) and observed total PCB concentrations in the water column.
- Time series plots of computed (estimated) and observed total PCB concentrations in the surficial sediments.
- Time series plots of computed (estimated) total PCB concentrations in the water column and sediments, versus observed fish body burdens.
- Longitudinal plots of computed and observed penta-PCB concentrations in the surficial sediments in the final year (2002) of the 74-year hindcast simulation.
- Time series plots of computed penta and (estimated) total PCB concentrations in the water column (organic carbon normalized) and observed values from dated sediment core slices.

Because reconstruction of historical penta-PCB loadings required many assumptions, and historical data were very sparse, computed results from the 74-year hindcast simulations were expressed as estimated uncertainty ranges instead of discrete trajectories. Interpretation of these results placed emphasis on broad trends and temporal structure,

2 Loadings and Forcing Functions

Daily loads of organic carbon and penta-PCB were estimated for each day of the 577 day continuous simulation period spanning September 1, 2001 through March 31, 2003 for relevant source categories, including:

- contaminated sites;
- non-point sources;
- point discharges;
- model boundaries
- tributaries
- atmospheric deposition; and
- CSOs

Table 2.1 outlines the various source categories, data, and methods used for computing the loads. Each of these computations is discussed in more detail in the sections that follow.

Table 2.1: Calculation Methods and Data for PCB and Carbon Loads to Delaware Estuary

Category	Method	Flows Available Data	PCBs Available Data	Carbon Available Data
NPDES Discharges				
Continuous Discharge	Product of daily flows and outfall specific mean (or measured) wet and mean (or measured) dry weather concentrations, toggled by precipitation data.	• Daily flow (facility specific) for dischargers in top ~90% of cumulative discharge. • Estimates of mean flows (facility specific) for dischargers outside top 90% of cumulative discharge flow.	Up to 4 wet weather and up to 4 dry weather samples per outfall	• For dischargers in top ~90% of cumulative discharge flow, daily POC concentrations estimated using daily facility specific TSS and BOD_5. All POC assumed to be PDC. • For dischargers outside top 90% of cumulative discharge flow mean POC concentrations estimated using the mean TSS and BOD_5 concentrations for all other facilities or literature values, depending on facility sub-category. All POC assumed to be PDC.
Industrial Stormwater Discharge	Product of daily runoff volumes calculated from daily precipitation totals and site hydrologic parameters; and site specific mean wet weather concentrations.	SCS Curve numbers, drainage areas, and time of concentration to estimate daily flows from precipitation data. Requested data from 20 facilities. 14 responded. DRBC estimated parameters for remaining 6.	Up to 4 wet weather samples per outfall	POC concentrations estimated from NURP data for TSS and assumed f_{oc}.

Table 2.1: Calculation Methods and Data for PCB and Carbon Loads to Delaware Estuary (Continued)

Category	Method	Flows Available Data	PCBs Available Data	Carbon Available Data
Tributaries and Boundaries				
Delaware River at Trenton	Product of gaged daily flows and concentration. For POC, concentration is estimated using rating curves defining a relationship with flow. For PCBs, concentration is the tributary specific mean wet and mean dry weather concentration, toggled by precipitation data.	Daily mean flow from the USGS gage at Trenton.	3 wet weather and 2 dry weather samples collected by USGS between 2000 and 2002.	Approximately 72 measurements of POC and DOC over a wide range of flows by USGS between 1991 and 2001.
Schuylkill River	Product of gaged daily flows and concentration. For POC, concentration is estimated using rating curves defining a relationship between flow and TSS and a 2nd relationship between TSS and POC. For PCBs, concentration is the tributary specific mean wet and mean dry weather concentration, toggled by precipitation data.	Daily mean flow from the USGS gage at Philadelphia.	3 wet weather and 3 dry weather samples collected by USGS between 2000 and 2002.	Approximately 20 POC measurements over a range of flows collected by USGS and Academy of Natural Sciences between 1998 and 2002.

Table 2.1: Calculation Methods and Data for PCB and Carbon Loads to Delaware Estuary (Continued)

Category	Method	Flows Available Data	PCBs Available Data	Carbon Available Data
Ocean Boundary	Flows (as calculated by hydrodynamic model using measured tide height and velocity data) and literature derived concentrations. Literature derived concentrations will be replaced with observed concentrations upon receipt of the data.	Tidal elevation and current from tide gages as processed by hydrodynamic model	Water column concentrations estimated from oyster and mussel tissue data using BCF. Awaiting measurements from 3 ocean boundary surveys during 2002 collected by DRBC.	POC measurements from 2 ocean boundary surveys during 2002 collected by DRBC and 18 particulate carbon measurements near mouth of the bay published by University of Delaware 1980 to present.
C&D Canal	Flows (as calculated by hydrodynamic model using measured tide height and velocity data) and concentrations.	Tidal elevation and current from tide gages as processed by hydrodynamic model	Water column concentrations estimated from one water column measurement by DRBC. Oyster and mussel tissue data using BCF also considered.	Mean of 2 water column measurements by DRBC. Paired TOC and DOC measurements at 3 stations in the C&D canal from 1995 to the present also considered.
Other Sampled Tributaries *(Brandywine, White Clay, Red Clay, Christina, Cooper, Pennsauken, Darby, Alloway, Frankford, Pennypack, Poquessing, Mantua, Big Timber, Crosswicks, Raccoon, Chester, Neshaminy, Rancocas, Salem)*	Product of gaged or extrapolated daily flows and tributary specific mean wet and mean dry weather concentrations, toggled by precipitation data.	Daily flow values at tributary sampling location extrapolated from upstream gage on same tributary or on a unit area basis from gage on a different stream with comparable geology and land use.	Typically 1 wet and 1 dry weather sample per tributary. Limited additional wet and dry weather sampling on selected tributaries.	Typically 1 wet and 1 dry weather sample per tributary. Limited additional wet and dry weather sampling on selected tributaries.

Table 2.1: Calculation Methods and Data for PCB and Carbon Loads to Delaware Estuary (Continued)

Category	Method	Flows Available Data	PCBs Available Data	Carbon Available Data
Non-sampled Tributaries	Product of gaged or extrapolated daily flows and mean wet and mean dry weather concentrations derived from sampled tributaries with lower concentrations, toggled by precipitation data. See Sections 2.3.5 and 2.4.5 for a detailed description.	Daily flow values at tributary mouth extrapolated from upstream gage on same tributary or on a unit area basis from gage on a different stream with comparable geology and land use. Upon satisfactory completion of non-point source estimation efforts, flows may be extrapolated only to the head of tide and non-point source loads will be applied between the sampling point and the mouth.	None. Concentrations estimated from mean of lower measurements on other 19 tributaries. Zone 6 tributary PCB loads are assumed to have already been accounted for using the Non-point source estimates, since all of the Zone 6 drainage area is currently within the non-point source drainage area.	None. Concentrations estimated from mean dry weather and mean wet weather of 19 sampled tributaries. In addition, some published data from University of Delaware available for tributaries in Zone 6.
Other External Loads				
CSOs	Product of daily CSO flows and WWTP specific mean wet weather influent concentrations. See Section 2.4.7 for a detailed description.	Daily flow values provided by Philadelphia and Delcora. Daily flows estimated for CCMUA and Wilmington (by DRBC) using relationships between measured flows and precipitation totals.	Influent PCB concentrations measured by higher flow facilities in 1999-2000. Philadelphia Southeast plant influent data may be unrepresentative of the usual concentrations. Southwest plant low influent also impacted. Philadelphia southeast plant data estimated as the mean of influent data from all other treatment plants (PWD-NE, Delcora, Wilmington, CCMUA). Philadelphia southwest plant estimated using high influent concentration only.	POC concentrations estimated from daily influent BOD_5 and TSS values provided by Philadelphia and Delcora. CCMUA and Wilmington influent data currently not provided - CCMUA and Wilmington plant influents estimated using Philadelphia data.

Table 2.1: Calculation Methods and Data for PCB and Carbon Loads to Delaware Estuary (Continued)

Category	Method	Flows Available Data	PCBs Available Data	Carbon Available Data
Non-point source by Broad Land Use	Product of daily runoff volumes calculated from daily precipitation totals and land use category hydrologic parameters and literature derived event mean concentrations. Rural-agricultural and wetland-adjacent water land use loads estimated from atmospheric deposition data and assumed pass-through rate.	Daily runoff volumes estimated from daily precipitation totals and site hydrologic characteristics.	Non-point source estimates being performed by CDM and DuPont. Literature value and range for event mean concentration (EMC) for urban and suburban land use categories. Sub-Basin specific atmospheric deposition data and assumed pass through rate for rural, agricultural, wetland, and adjacent water land uses.	Estimated from EPA runoff database mean concentration for TSS and assumed f_{oc}.
Facility / site specific non-point source loads	Site PCB load calculated as the product of areal solids yield estimates and site soil PCB concentrations. Tasked to various federal and state agencies for completion.	N/A	Wide Range of data availability from site to site.	N/A

Table 2.1: Calculation Methods and Data for PCB and Carbon Loads to Delaware Estuary (Continued)

Category	Method	Flows Available Data	PCBs Available Data	Carbon Available Data
Marsh and Wetland Areas	Estimated daily areal loading rate of particulate carbon as grams C / m^2 / day from literature.	N/A	N/A	• Academy of Natural Sciences, "Impact of AquaticVegetation on Water Quality of the Delaware River Estuary", (1998); • Neubauer et al. (2000); • Neubauer et al. (2001); • Cerco, Chesapeake Bay Water Quality Model (draft).
Atmospheric Deposition				
Atmospheric Wet and Dry Deposition	• Dry deposition, seasonally by zone; • Wet deposition, single precip aqueous concentration value by zone; • Gaseous concentration, single temperature dependent spatially variable formula.	N/A	• Rutgers University atmospheric particulate concentrations at ~6 stations over ~30 sampling events in 2002; • Rutgers University atmospheric gaseous concentrations at ~7 stations over ~30 sampling events in 2002.	Measured atmospheric total particulate concentrations and f_{oc} at ~7 stations over ~30 sampling events in 2002.

2.2 Daily Flow Estimates

In most cases, the first step estimating the daily loads required estimation of daily flow. The sections below discuss daily flow estimates in more detail.

2.2.1 Point Discharges

A cumulative flow distribution curve was developed for 144 discharges using existing effluent design flow values, to determine which dischargers contributed the majority of the flow. From that analysis, those discharges contributing to the 90% cumulative flow were asked to submit daily flow measurements for the continuous simulation period from September 1, 2001 through March 31, 2003. For dischargers contributing the remaining 10% of flow, daily flow values were estimated using the mean flow reported in the Permit Compliance System (PCS) for the continuous simulation period, where available. Daily flows for dischargers who had not submitted data to PCS during the simulation period were estimated using previous effluent design flow values, permit design capacity, or a placeholder value. A placeholder flow value of 0.1 MGD was used for six outfalls for which no other data was available. As shown in Table 2.2, flows estimated using a placeholder value made up less than one tenth of one percent of the total point discharge flow.

For discharges consisting primarily of stormwater runoff, dischargers were asked to submit (1) the drainage area for each outfall, (2) the composite runoff curve number for the drainage area; and (3) the time of concentration, in accordance with the document *Urban Hydrology for Small Watersheds, Technical Release 55,* Soil Conservation Service (currently, Natural Resources Conservation Service), June 1986. These inputs were used by the Commission to compute runoff volume estimates from precipitation data. For dischargers who failed to respond, site parameters were estimated by DRBC staff using digital aerial photos, USGS quad maps, and site descriptions. For stormwater discharges with a continuous base flow, daily flows were estimated by extrapolating from nearby similar gaged watersheds, on a flow per unit area basis.

Discharges consisting of primarily non-contact cooling water were assigned a zero flow value. Loads from non-contact cooling water were assumed, in this iteration, to be negligible.

Table 2.2 shows the percentage of total flow associated with each method used to estimate daily flow. Table 2.3 shows the percentage of point discharge flow associated with the sub categories of municipal waste water treatment, industrial process effluent, and industrial stormwater runoff.

Table 2.2: Flow Estimation Category and % of Total Flow

Flow Estimation Category	% of Total Flow
Daily supplied by discharger	87.11%
Estimated from PCS data during the simulation period	11.57%
Effluent Design Flow	0.79%
Permit Design Capacity	0.44%
Placeholder value (0.1 mgd)	0.06%
Stormwater Runoff estimated from SCS data	0.02%
By similar watersheds for ditches with baseflow	0.01%
Non-Contact Cooling Water (Zeroed out)	0.00%

Table 2.3: Percentage of Point Discharge Flow by Sub Category

Point Discharge Sub Category	Percentage of Total Point Discharge Flow
Municipal Waste Water Treatment	86.92%
Industrial Process Effluent	13.06%
Industrial Stormwater Runoff	0.02%

2.2.2 Delaware at Trenton

Daily flow measurements for USGS gage 01463500 are available from 1912 until present, and provide discharge flows from the 6,780 sm. Delaware drainage basin. Mean daily flow values from September 1 2001 through March 31, 2003, were utilized as described in the following sections.

2.2.3 Schuylkill

Daily flow measurements for USGS gage 01474500 are available from 1931 until present, and provide discharge flows from the 1,893 sm. Schuylkill drainage basin. Mean daily flow values from September 1 2001 through March 31, 2003, were utilized as described in the following sections.

2.2.4 Tributaries

Tributary flows in the Estuary portion of the Delaware River were taken from existing USGS gages when available and extrapolated from nearby streams when stream gages were not available. The USGS maintains many gages in the Delaware River Basin and provides flow information via its web site, NWISWeb Data for the Nation (http://waterdata.usgs.gov/nwis/discharge).

The majority of stream flow into the Estuary is from the Delaware River at Trenton and the Schuylkill River at Philadelphia. The gages at these two locations provide long-term daily flow information to the estuary. Many of the smaller streams provide daily flow information and can be used to extrapolate flow for streams which are not gaged. Flow was extrapolated for streams without gages by using the nearest appropriate gage to extrapolate flows on a unit area basis. Selection of gaged streams used for extrapolation was based primarily on underlying geology. Drainage areas for streams without gages and for drainage areas downstream of gaging station were calculated using Geographic Information System (GIS) methods. For loading calculations and input to the model, flows were extrapolated, as appropriate, to tributary water quality sampling locations.

Table 2.4: Tributary Flow Gages and Extrapolation Index

Tributary	Gage	Extrapolated from (if not gaged)
Alloways	Not gaged	Raccoon
Assunpink	01464000	
Big Timber	Not gaged	Cooper
Brandywine	01481500	
Broadkill	Not gaged	St. Jones
Cedar	Not gaged	St. Jones
Chester	01477000	
Christina	01478000	
Cohansey	Not gaged	Maurice
Cooper	01467150	
Crosswicks	01464500	
Crum	01475850	
Darby	Not gaged	Chester
Frankford	01467087	
Leipsic	Not gaged	St. Jones
Mantua	Not gaged	Raccoon
Maurice	01411500	
Mispillion	Not gaged	St. Jones
Muderkill	Not gaged	St. Jones
Neshaminy	01465500	
Newton	Not gaged	Cooper
Pennypack	01467048	
Pennsauken	Not gaged	Cooper
Poquessing	01465798	
Raccoon	01477120	
Rancocas	01467000	
Red Clay	01480015	
Salem	01482500	
Smyrna	Not gaged	St. Jones

Table 2.4: Tributary Flow Gages and Extrapolation Index (*continued*)

Tributary	Gage	Extrapolated from (if not gaged)
St. Jones	01483700	
Stowe	Not gaged	Maurice
White Clay	01479000	

Table 2.5: Relative Flow Contribution of Tributaries to the Delaware Estuary

Flow Source	%of total Flow
Delaware River at Trenton	55%
Schuylkill River at Philadelphia	14%
All other gaged tributaries	9%
Non-gaged tributaries and direct drainage areas	22%

2.3 Carbon Load Estimates

Three forms of carbon are included in the model. They are dissolved organic carbon (DOC), particulate detrital carbon (PDC) and biotic carbon (BIC). DOC represents microparticulates (colloids) and macromolecules that cannot be separated from whole water samples by conventional filtration or centrifugation. PDC represents non-living particulate detrital carbon derived from varied sources including phytoplankton decomposition, zooplankton excretion, point discharge effluents, and small scale decaying vegetative matter. BIC represents particulate organic carbon contained in live phytoplankton biomass. Since DOC concentrations for the model were specified rather than computed, no DOC loading estimates were performed. In our model, Particulate Organic Carbon consists of only two sub fractions: BIC and PDC.

$$POC = BIC + PDC$$

Similarly, the sum of POC and DOC yields Total Organic Carbon (TOC).

$$TOC = POC + DOC$$

PDC and BIC loading estimates were performed for various source categories as described in the following sections. Figure 2.1 shows a comparison of the PDC load from each source category in the system. The “Boundary” category consists of PDC load from the Delaware at Trenton and the Schuylkill Rivers. It should be noted that, in the context of the model, the Delaware at Trenton and the Schuylkill are boundaries with assigned daily concentrations, as opposed to loads. They are included here for purposes of comparison.

Figure 2.1 - PDC load by Source Category During the 577 Day Simulation Period

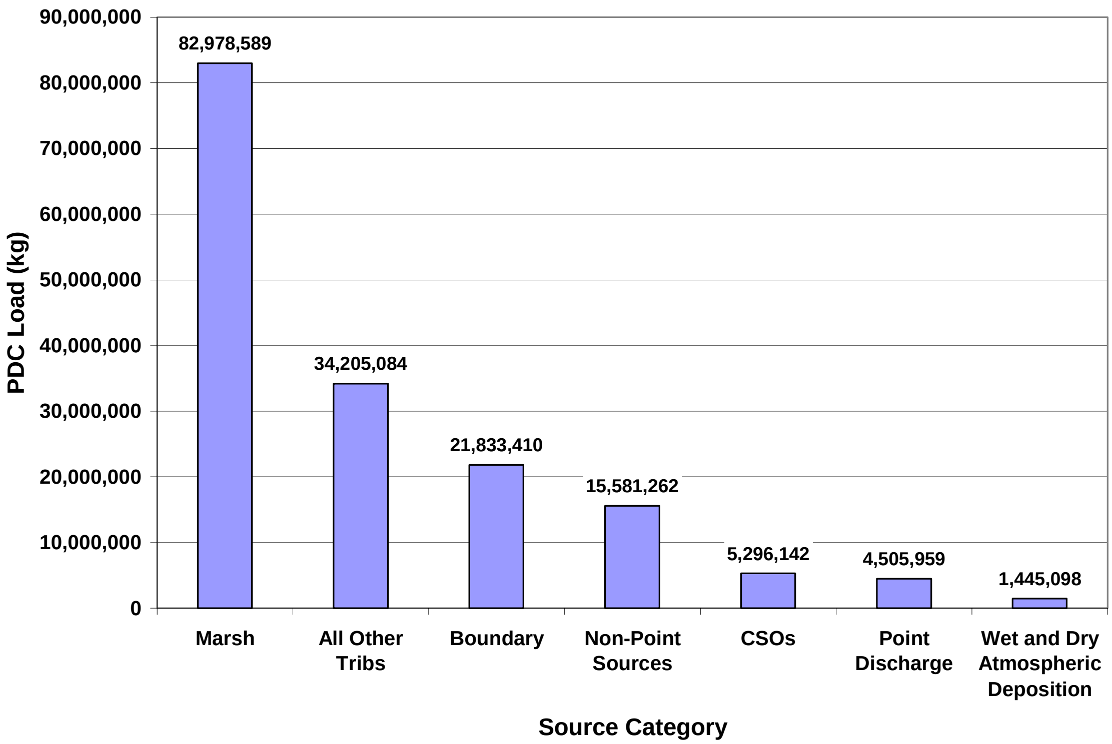


Figure 2.2 shows a comparison of the BIC load from each source category in the system. Again, the “Boundary” category refers to the Delaware at Trenton and the Schuylkill Rivers, and is not strictly a load. The term “Internal BIC Load” refers to carbon generated within the water column through primary production or the reproduction and growth of phytoplankton.

Figure 2.2 - BIC load by Source Category During the 577 Day Simulation Period

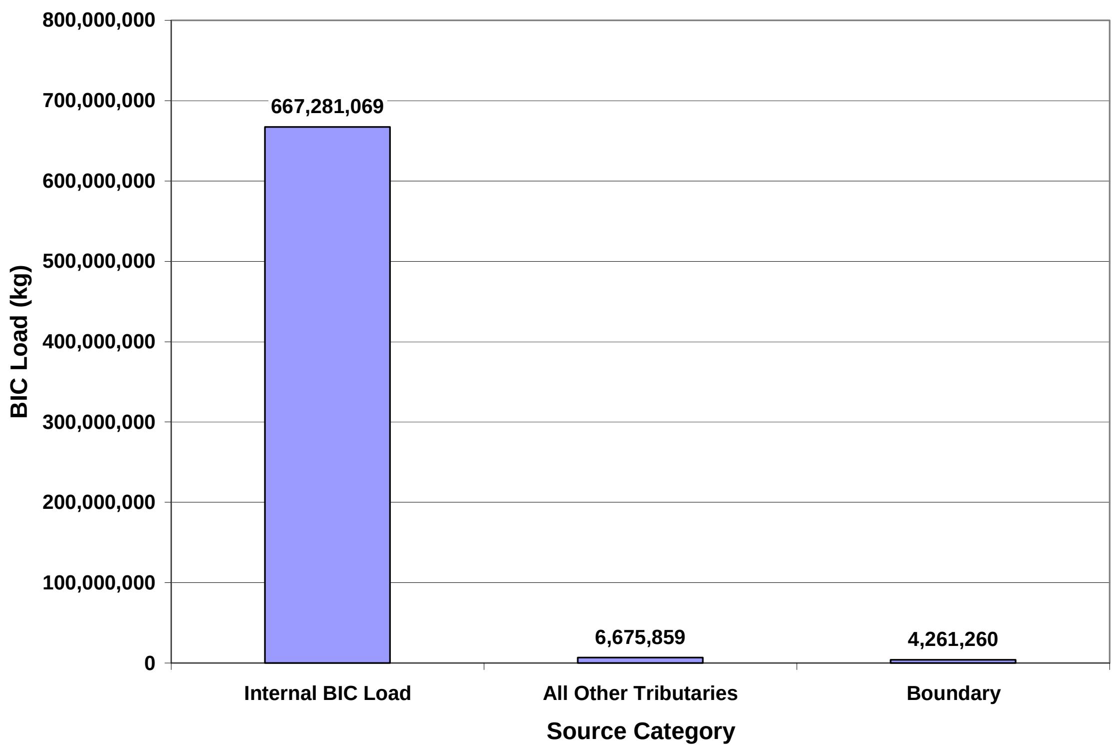


Figure 2.3 shows a comparison of BIC and PDC load for each zone. These loads include the boundary contributions from the Delaware at Trenton, into Zone 2, and the Schuylkill, into Zone 4. It should be noted that while the BIC load is larger overall, PDC is a larger proportion of POC in Zones 2 through 5. The larger proportion of BIC in Zone 6 is due to the large surface area, and therefore high primary production, in Zone 6, as shown in Figure 2.4.

Figure 2.3 - 577 Day BIC and PDC Load for Each Zone

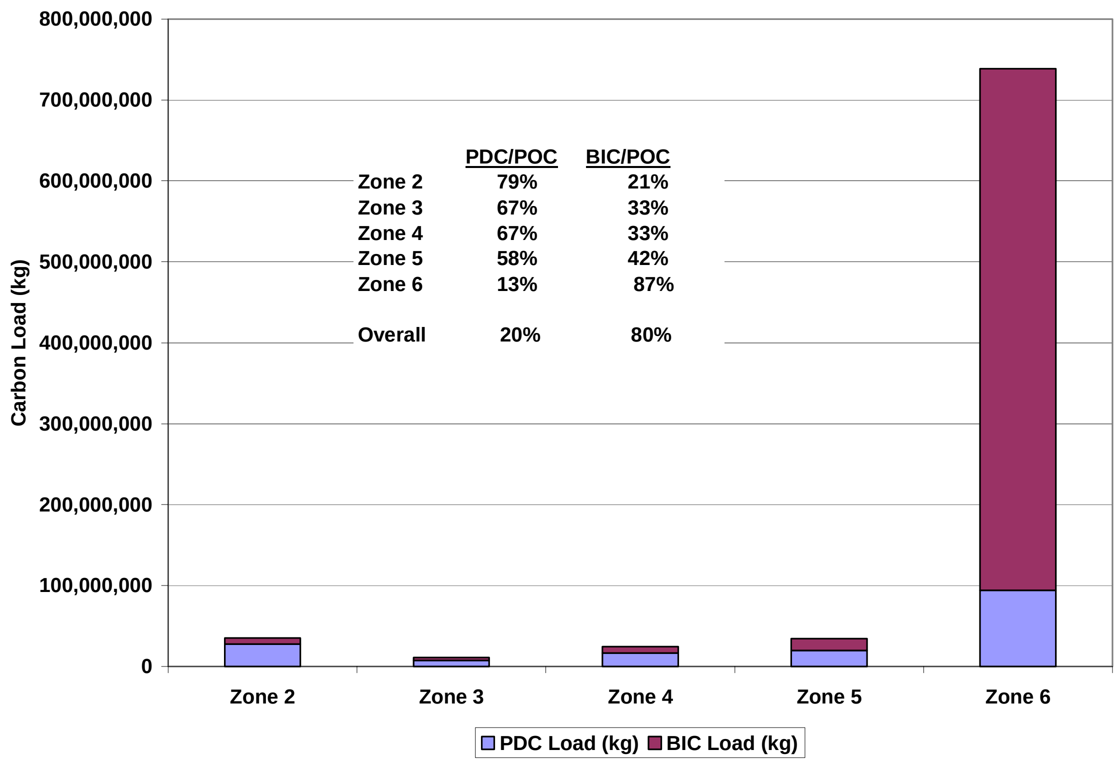
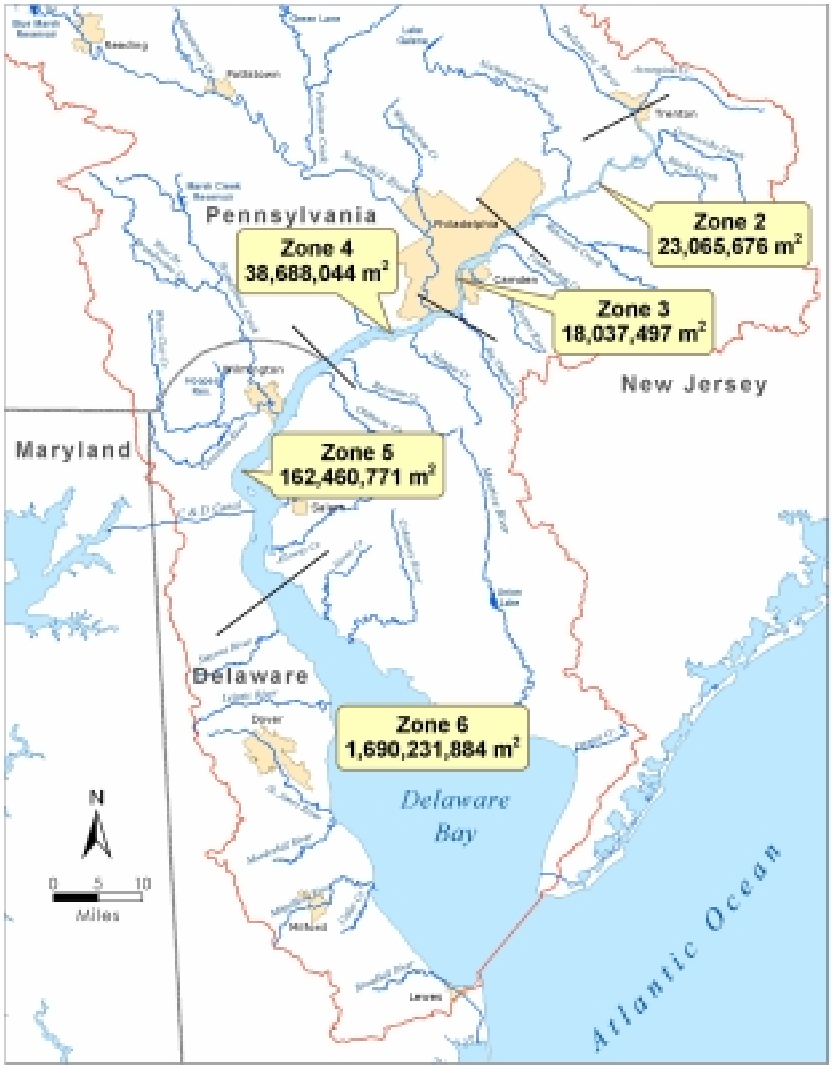


Figure 2.4 - Map of the Delaware Estuary Including Surface Area by Zone



2.3.2 Carbon to Chlorophyll Ratio

In order to separate measured POC into PDC and BIC fractions, we needed an estimate of the carbon to chlorophyll ratio for the Delaware estuary. The Carbon to Chlorophyll ratio provides an estimate of the portion of BIC from measured POC, as shown below:

$$Chl \times \left(C/_{Chl} \right) = BIC$$

and

$$POC - BIC = PDC$$

where:

Chl	=	Chlorophyll-a (mg/L)
C/Chl	=	Carbon to chlorophyll ratio
BIC	=	Biotic Carbon (mg/L)
POC	=	Particulate Organic Carbon (mg/L)
PDC	=	Particulate Detrital Carbon (mg/L)

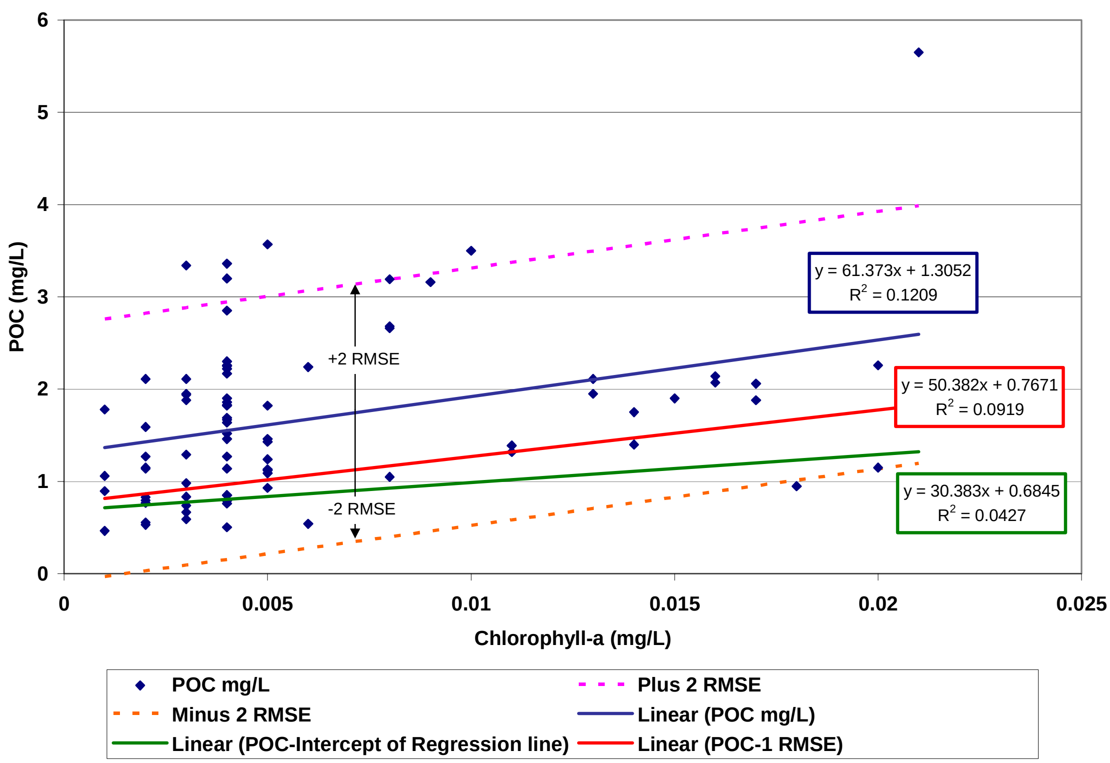
In order to estimate an appropriate *C/Chl* for the Delaware estuary, we compiled available paired measurements of POC and chlorophyll-a, as shown in Table 2.4, and computed resultant BIC values associated with each assumed *C/Chl* and measured POC. We used two metrics to assess the appropriateness of each assumed *C/Chl*. First, the selected *C/Chl* should not result in BIC values greater than the measured POC, since BIC is a subset of POC. Second, the selected *C/Chl* should result in a BIC concentration that is roughly 15 to 25% of the POC concentration. Table 2.4 shows that *C/Chl* values between 30 and 50 generally satisfy these criteria.

Table 2.6: Assessment of Paired POC and Chlorophyll-a Measurements to Estimate Carbon to Chlorophyll Ratio

				C/Chl. Ratio	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**	**55**	**60**	**100**	**110**	**150**
				Number of cases where BIC>POC	0	0	0	0	0	0	0	0	0	0	1	2	3	4	15
				Mean BIC/POC	2.04%	4.08%	6.13%	8.17%	10.21%	12.25%	14.29%	16.33%	18.38%	20.42%	22.46%	24.50%	40.84%	44.92%	61.25%
Date	Station	POC mg/L	Chl-A ug/L	Chl-A mg/L	Calculated BIC (mg/L)														
3/15/2002	1	3.1600	9.0	0.009	0.045	0.09	0.135	0.18	0.225	0.27	0.315	0.36	0.405	0.45	0.495	0.54	0.9	0.99	1.35
3/15/2002	2	2.2600	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
3/15/2002	3	2.8500	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
3/15/2002	4	3.2000	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
3/15/2002	5	2.2400	6.0	0.006	0.03	0.06	0.09	0.12	0.15	0.18	0.21	0.24	0.27	0.3	0.33	0.36	0.6	0.66	0.9
3/15/2002	6	2.6600	8.0	0.008	0.04	0.08	0.12	0.16	0.2	0.24	0.28	0.32	0.36	0.4	0.44	0.48	0.8	0.88	1.2
3/15/2002	7	2.6800	8.0	0.008	0.04	0.08	0.12	0.16	0.2	0.24	0.28	0.32	0.36	0.4	0.44	0.48	0.8	0.88	1.2
3/15/2002	8	2.0600	17.0	0.017	0.085	0.17	0.255	0.34	0.425	0.51	0.595	0.68	0.765	0.85	0.935	1.02	1.7	1.87	2.55
3/15/2002	9	2.2600	20.0	0.02	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1	1.1	1.2	2	2.2	3
3/15/2002	10	2.0700	16.0	0.016	0.08	0.16	0.24	0.32	0.4	0.48	0.56	0.64	0.72	0.8	0.88	0.96	1.6	1.76	2.4
3/15/2002	11	1.8800	17.0	0.017	0.085	0.17	0.255	0.34	0.425	0.51	0.595	0.68	0.765	0.85	0.935	1.02	1.7	1.87	2.55
3/15/2002	12	1.7500	14.0	0.014	0.07	0.14	0.21	0.28	0.35	0.42	0.49	0.56	0.63	0.7	0.77	0.84	1.4	1.54	2.1
3/15/2002	13	1.1300	5.0	0.005	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.225	0.25	0.275	0.3	0.5	0.55	0.75
3/15/2002	14	0.7700	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
3/15/2002	15	0.5920	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
4/11/2002	1	3.3600	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
4/11/2002	2	2.1700	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
4/11/2002	3	1.4300	5.0	0.005	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.225	0.25	0.275	0.3	0.5	0.55	0.75
4/11/2002	4	1.3200	11.0	0.011	0.055	0.11	0.165	0.22	0.275	0.33	0.385	0.44	0.495	0.55	0.605	0.66	1.1	1.21	1.65
4/11/2002	5	1.4000	14.0	0.014	0.07	0.14	0.21	0.28	0.35	0.42	0.49	0.56	0.63	0.7	0.77	0.84	1.4	1.54	2.1
4/11/2002	6	2.1100	13.0	0.013	0.065	0.13	0.195	0.26	0.325	0.39	0.455	0.52	0.585	0.65	0.715	0.78	1.3	1.43	1.95
4/11/2002	7	1.9000	15.0	0.015	0.075	0.15	0.225	0.3	0.375	0.45	0.525	0.6	0.675	0.75	0.825	0.9	1.5	1.65	2.25
4/11/2002	8	2.1400	16.0	0.016	0.08	0.16	0.24	0.32	0.4	0.48	0.56	0.64	0.72	0.8	0.88	0.96	1.6	1.76	2.4
4/11/2002	9	1.9500	13.0	0.013	0.065	0.13	0.195	0.26	0.325	0.39	0.455	0.52	0.585	0.65	0.715	0.78	1.3	1.43	1.95
4/11/2002	10	1.3900	11.0	0.011	0.055	0.11	0.165	0.22	0.275	0.33	0.385	0.44	0.495	0.55	0.605	0.66	1.1	1.21	1.65
4/11/2002	11	1.0500	8.0	0.008	0.04	0.08	0.12	0.16	0.2	0.24	0.28	0.32	0.36	0.4	0.44	0.48	0.8	0.88	1.2
4/11/2002	12	0.8520	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
4/11/2002	13	0.7960	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
4/11/2002	14	0.5560	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
4/11/2002	15	0.5310	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
4/22/2002	1	5.6500	21.0	0.021	0.105	0.21	0.315	0.42	0.525	0.63	0.735	0.84	0.945	1.05	1.155	1.26	2.1	2.31	3.15
4/22/2002	2	3.5000	10.0	0.01	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5	0.55	0.6	1	1.1	1.5
4/22/2002	3	3.1900	8.0	0.008	0.04	0.08	0.12	0.16	0.2	0.24	0.28	0.32	0.36	0.4	0.44	0.48	0.8	0.88	1.2
4/22/2002	4	3.5700	5.0	0.005	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.225	0.25	0.275	0.3	0.5	0.55	0.75
4/22/2002	5	1.0900	5.0	0.005	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.225	0.25	0.275	0.3	0.5	0.55	0.75
4/22/2002	6	1.1200	5.0	0.005	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.225	0.25	0.275	0.3	0.5	0.55	0.75
4/22/2002	7	0.9310	5.0	0.005	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.225	0.25	0.275	0.3	0.5	0.55	0.75
4/22/2002	8	0.7900	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
4/22/2002	9	1.2400	5.0	0.005	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.225	0.25	0.275	0.3	0.5	0.55	0.75
4/22/2002	10	1.4600	5.0	0.005	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.225	0.25	0.275	0.3	0.5	0.55	0.75
4/22/2002	11	1.1400	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
4/22/2002	12	1.2700	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
4/22/2002	13	1.9400	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
4/22/2002	14	1.1500	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
4/22/2002	15	0.8340	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
6/19/2002	1	3.3400	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
6/19/2002	2	1.8200	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
6/19/2002	3	1.6700	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
6/19/2002	4	1.2700	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
6/19/2002	5	0.7390	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
6/19/2002	6	0.7600	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
6/19/2002	7	0.6660	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
6/19/2002	8	0.9810	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
6/19/2002	9	1.9500	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
6/19/2002	10	0.8310	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
6/19/2002	11	2.1100	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
6/19/2002	12	1.5900	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
6/19/2002	13	1.7800	1.0	0.001	0.005	0.01	0.015	0.02	0.025	0.03	0.035	0.04	0.045	0.05	0.055	0.06	0.1	0.11	0.15
6/19/2002	14	0.8960	1.0	0.001	0.005	0.01	0.015	0.02	0.025	0.03	0.035	0.04	0.045	0.05	0.055	0.06	0.1	0.11	0.15
6/19/2002	15	1.0600	1.0	0.001	0.005	0.01	0.015	0.02	0.025	0.03	0.035	0.04	0.045	0.05	0.055	0.06	0.1	0.11	0.15
10/8/2002	1	1.8800	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
10/8/2002	2	2.1100	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
10/8/2002	3	2.2500	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
10/8/2002	4	2.3000	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
10/8/2002	5	1.8200	5.0	0.005	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.225	0.25	0.275	0.3	0.5	0.55	0.75
10/8/2002	6	1.6900	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
10/8/2002	7	2.2200	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
10/8/2002	8	1.5200	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
10/8/2002	9	1.8300	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
10/8/2002	10	1.6400	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
10/8/2002	11	1.8600	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
10/8/2002	12	1.4600	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
10/8/2002	13	1.2900	3.0	0.003	0.015	0.03	0.045	0.06	0.075	0.09	0.105	0.12	0.135	0.15	0.165	0.18	0.3	0.33	0.45
10/8/2002	14	1.1400	2.0	0.002	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.11	0.12	0.2	0.22	0.3
10/8/2002	15	0.4650	1.0	0.001	0.005	0.01	0.015	0.02	0.025	0.03	0.035	0.04	0.045	0.05	0.055	0.06	0.1	0.11	0.15
9/23/2002	SBS	0.5420	6.0	0.006	0.03	0.06	0.09	0.12	0.15	0.18	0.21	0.24	0.27	0.3	0.33	0.36	0.6	0.66	0.9
9/23/2002	SJFS	1.1500	20.0	0.02	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1	1.1	1.2	2	2.2	3
9/23/2002	EOC	0.9480	18.0	0.018	0.09	0.18	0.27	0.36	0.45	0.54	0.63	0.72	0.81	0.9	0.99	1.08	1.8	1.98	2.7
9/23/2002	SJL	0.5050	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
9/23/2002	LP	0.8500	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6
9/23/2002	RI	1.9000	4.0	0.004	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.24	0.4	0.44	0.6

To further narrow the choice for *C/Chl*, we plotted the measured POC versus measured Chlorophyll-a, along with regression line, and the regression line ± 2 root mean square error (RMSE) of the regression, as shown in Figure 2.5. In addition, we computed two new regression lines based on adjusted POC values, to assess the likely range of the slope for POC vs. chlorophyll-a. For the first adjustment, we subtracted the intercept of the regression line from the POC data and regressed those adjusted values (green line). For the second adjustment, we subtracted one RMSE from the POC data and regressed those adjusted values (red line) as well. Adjusted data points are not shown in Figure 2.5, only the resultant regression lines. For both adjustments, negative values of POC were not included in the regressions. Although BIC is a subset of POC, the slope of BIC vs. Chlorophyll-a, which is *C/Chl*, will be equal to the slope of POC vs. chlorophyll-a since we consider BIC/POC to be constant. Therefore, Figure 2.5 further suggests a range between approximately 30 and 60 for *C/Chl*. Ultimately, we selected a value of 40 for *C/Chl* because it consistently fell centrally within the bounds of all the metrics used. Recognizing that there is some uncertainty associated with *C/Chl*, model calibration targets typically included PDC and BIC values computed from *C/Chl* values of 30, 40, and 50, to express the likely range.

Figure 2.5 - Regression of POC Vs. Chlorophyll-a Data with ± 2 RMSE and 2 Adjustments



2.3.3 Internal Biotic Carbon Generation

Internal generation of BIC was estimated using the long term primary production measurements made by Dr. Jonathan Sharpe in the Delaware Estuary since 1978. Dr. Sharpe provided representative long term average primary production estimates to DRBC for 5 seasons including an early spring period (Spring 1) and late spring period (Spring 2) as well as 22 spatial ranges, as shown in Tables 2.5 and 2.6, below.

Table 2.7: Definition of Seasons for Internal Carbon Production

Dates	Season
November 17 - February 28	Winter
March 1 – April 11	Spring 1
April 12 – May 10	Spring 2
May 11 – September 12	Summer
September 13 – November 16	Fall

Table 2.8: Internal Seasonal Carbon Production by Zone (kg C / m^2 / day)

Range (River Miles)	Spring 1	Spring 2	Summer	Fall	Winter
Below 0	4.37E-04	4.37E-04	9.60E-04	2.82E-04	2.70E-04
0 to 6.21	6.86E-04	6.86E-04	1.60E-03	9.43E-04	2.87E-04
6.21 to 12.42	6.53E-04	6.53E-04	1.51E-03	3.59E-04	2.06E-04
12.42 to 18.64	1.14E-03	1.14E-03	2.11E-03	3.26E-04	4.51E-04
18.64 to 24.85	1.37E-03	1.37E-03	1.88E-03	2.93E-04	3.89E-04
24.85 to 31.06	1.49E-03	1.49E-03	1.36E-03	3.09E-04	3.27E-04
31.06 to 37.27	1.28E-03	1.28E-03	1.12E-03	1.04E-04	1.99E-04
37.27 to 43.48	7.58E-04	7.58E-04	8.01E-04	1.16E-04	1.44E-04
43.48 to 49.7	4.40E-04	4.40E-04	5.77E-04	5.92E-05	4.09E-05
49.7 to 55.91	2.95E-04	2.95E-04	5.50E-04	7.13E-05	5.14E-05
55.91 to 62.12	2.02E-04	2.02E-04	3.31E-04	4.42E-05	2.76E-05
62.12 to 68.33	1.36E-04	1.36E-04	3.83E-04	9.04E-05	1.07E-05
68.33 to 74.55	1.27E-04	1.27E-04	4.06E-04	5.72E-05	6.48E-06
74.55 to 80.76	2.83E-04	2.83E-04	6.34E-04	9.95E-05	1.06E-05
80.76 to 86.97	3.30E-04	3.30E-04	9.70E-04	1.74E-04	1.10E-05
86.97 to 93.18	5.10E-04	5.10E-04	9.87E-04	1.02E-04	1.39E-05
93.18 to 99.39	2.56E-04	2.56E-04	1.19E-03	1.68E-04	1.08E-05
99.39 to 105.61	2.62E-04	2.62E-04	1.18E-03	2.74E-04	7.56E-06
105.61 to 111.82	2.07E-04	2.07E-04	1.38E-03	1.29E-04	1.02E-05
111.82 to 118.03	3.26E-04	3.26E-04	1.30E-03	2.46E-04	1.46E-05
118.03 to 124.24	1.90E-04	1.90E-04	1.60E-03	1.80E-04	1.23E-05
Above 124.24	1.65E-04	1.65E-04	9.57E-04	3.68E-05	8.64E-06

2.3.4 Marsh Carbon Loads

In order to estimate the carbon load from marshes in the Delaware Estuary, DRBC consulted available literature for estimates of carbon production and export. The Academy of Natural Sciences (ANS) estimated a range of biomass production for emergent aquatic vegetation (EAV) in the Delaware Estuary between 241 g m^{-2} yr^{-1} for low marsh to 1305 g m^{-2} yr^{-1} for high marsh. The ANS report cites estimates of low marsh EAV production rates on the New Jersey side of the Delaware River of 863 g m^{-2} yr^{-1} by McCormick (1977) and 780 g m^{-2} yr^{-1} by Wingham and Simpson (1975). The ANS report also cites high marsh EAV production estimates ranging from 940 g m^{-2} yr^{-1}

by Wingham and Simpson (1976) to 1600 g m^{-2} yr^{-1} Good and Good (1975). Combined with the ANS measured carbon proportion of approximately 40%, this results in a range of carbon production between 96.4 and 640 g C m^{-2} yr^{-1}.

Estimates of carbon export, or flux, were more limited than estimates of production. Lotrich et al., (1979) as cited in Nixon (1980) estimated the annual *flux* of organic carbon between salt marsh and coastal water at Canary Creek, Lewes, Del at 100 g TOC m^{-2} yr^{-1} with 62 g POC m^{-2} yr^{-1} and 38 g DOC m^{-2} yr^{-1}.

In other systems, Neubauer et al. (2000) measured a range of annual net macrophyte production in a tidal freshwater marsh (Pamunkey River) of 1.4 - 2 g C m^{-2} day^{-1}. This would correspond to a range of 511 – 730 g C m^{-2} yr^{-1}, which is reasonably comparable with the ranges cited for the Delaware Estuary. In order to estimate a flux from this carbon production rate, Cerco (2002 draft) assumed that carbon production represents an absolute upper bound for export, and assumed an export value of 0.3 g C m^{-2} day^{-1} for the 2nd Generation Chesapeake Bay Water Quality Model. Cerco also assumed that ⅓of the exported carbon was in the form of DOC, ⅓ was in the form of labile particulate carbon, and ⅓ was in form of refractory particulate carbon. Since the definitions of labile and refractory particulate carbon differ from our definition of particulate detrital carbon, we assume that Cerco's export rate should correspond to a value between 0.1 and 0.2 g PDC m^{-2} day^{-1}, which again agrees reasonably well with a flux estimate of 0.17 g POC m^{-2} day^{-1} by Lotrich et al. for marshes in Canary Creek in Lewes, Delaware.

For this iteration, we used a loading rate of 0.15 g PDC m^{-2} day^{-1} from marshes. We assumed that the marsh load consisted entirely of PDC as opposed to BIC. Marsh areas in each zone were obtained from USGS National Hydrography Dataset GIS coverages. Marsh loads were totaled for each zone and loaded into individual mainstem model segments using the relative area of the segment as a weighting factor, thus preventing inappropriately high loading rates to smaller segments. Based on observations that marsh particulate carbon is typically only available when marshes become inundated or during significant storm events, the marsh carbon load was pulsed into the system assuming 60% of the total load was released during spring tides, and 40% was released during storm events. Of the 40% released during storm events, the precipitation total for a 24 hour period divided by the total for 577 days was used as a weighting factor to distribute the storm released PDC. Thus larger storm events would release more PDC than small storm events. Similarly, on days with concurrent spring tides and storm events, both the tidal and storm portions of the PDC load were released.

2.3.5 Tributary Carbon Loads

Tributary carbon loads were estimated as the product of gaged or extrapolated daily flows and tributary specific mean wet and mean dry weather concentrations, toggled by precipitation data. The tributary specific mean dry weather concentration was used for any day with a 24-hour rainfall total less than 0.1-inch, and the tributary specific mean wet weather concentration was used for any day with a 24-hour rainfall total of 0.1-inch or more. Table 2.7 below shows the measured POC concentrations during the simulation period.

Table 2.9: Summary of Tributary POC Measurements

Tributary	Date	RESULT	UNITS	BIC	PDC
Alloways Creek	7/16/2002	6.63	mg/L	1.08	5.55
Alloways Creek	12/13/2002	2.63	mg/L	0.43	2.20
Big Timber Creek	6/7/2002	0.91	mg/L	0.15	0.76
Big Timber Creek	7/18/2002	1.12	mg/L	0.18	0.94
Big Timber Creek	10/7/2002	1.35	mg/L	0.22	1.13
Big Timber Creek	12/10/2002	1.57	mg/L	0.26	1.31
Brandywine Creek	7/18/2002	0.22	mg/L	0.04	0.19
Brandywine Creek	8/29/2002	0.50	mg/L	0.08	0.41
Brandywine Creek	12/12/2002	21.20	mg/L	3.46	17.74
Brandywine Creek	12/16/2002	0.87	mg/L	0.14	0.73
Chester Creek	7/17/2002	0.37	mg/L	0.06	0.31
Chester Creek	12/10/2002	0.96	mg/L	0.16	0.80
Christina River	7/18/2002	0.62	mg/L	0.10	0.52
Christina River	8/29/2002	7.46	mg/L	1.22	6.24
Christina River	10/8/2002	0.52	mg/L	0.09	0.44
Christina River	11/12/2002	1.80	mg/L	0.29	1.51
Christina River	12/16/2002	0.92	mg/L	0.15	0.77
Christina River	12/20/2002	15.90	mg/L	2.60	13.30
Cooper River	8/1/2002	4.14	mg/L	0.68	3.46
Cooper River	10/7/2002	4.91	mg/L	0.80	4.11
Cooper River	12/10/2002	0.89	mg/L	0.15	0.75
Cooper River	2/22/2003	1.74	mg/L	0.28	1.46
Crosswicks Creek	5/13/2002	2.33	mg/L	0.38	1.95
Crosswicks Creek	7/16/2002	1.14	mg/L	0.19	0.95
Crosswicks Creek	10/7/2002	0.34	mg/L	0.06	0.29
Crosswicks Creek	10/31/2002	2.36	mg/L	0.39	1.97
Crosswicks Creek	12/10/2002	0.87	mg/L	0.14	0.73
Crosswicks Creek	3/6/2003	4.34	mg/L	0.71	3.63
Crosswicks Creek	3/27/2002	10.50	mg/L	1.71	8.79
Darby Creek	7/17/2002	1.11	mg/L	0.18	0.93
Darby Creek	10/8/2002	1.35	mg/L	0.22	1.13
Darby Creek	11/12/2002	1.33	mg/L	0.22	1.11
Darby Creek	12/10/2002	0.98	mg/L	0.16	0.82
Frankford Creek	4/25/2002	26.90	mg/L	4.39	22.51
Frankford Creek	7/17/2002	1.81	mg/L	0.30	1.51
Frankford Creek	12/10/2002	1.26	mg/L	0.21	1.05
Mantua Creek	5/18/2002	4.38	mg/L	0.72	3.66
Mantua Creek	7/16/2002	3.28	mg/L	0.54	2.74
Mantua Creek	10/7/2002	1.80	mg/L	0.29	1.51

Table 2.9: Summary of Tributary POC Measurements (continued)

Tributary	Date	RESULT	UNITS	BIC	PDC
Mantua Creek	11/6/2002	1.11	mg/L	0.18	0.93
Mantua Creek	12/10/2002	1.82	mg/L	0.30	1.52
Neshaminy Creek	4/26/2002	0.58	mg/L	0.09	0.48
Neshaminy Creek	5/9/2002	0.64	mg/L	0.10	0.54
Neshaminy Creek	7/17/2002	0.39	mg/L	0.06	0.33
Neshaminy Creek	12/10/2002	0.43	mg/L	0.07	0.36
Pennsauken Cr.	8/1/2002	0.84	mg/L	0.14	0.70
Pennsauken Cr.	12/10/2002	1.96	mg/L	0.32	1.64
Pennypack Creek	4/25/2002	3.04	mg/L	0.50	2.54
Pennypack Creek	7/17/2002	0.22	mg/L	0.04	0.19
Pennypack Creek	12/10/2002	0.37	mg/L	0.06	0.31
Poquessing Creek	4/25/2002	4.02	mg/L	0.66	3.36
Poquessing Creek	7/17/2002	0.38	mg/L	0.06	0.31
Poquessing Creek	12/10/2002	0.34	mg/L	0.06	0.29
Raccoon Creek	5/18/2002	13.30	mg/L	2.17	11.13
Raccoon Creek	7/16/2002	3.10	mg/L	0.51	2.59
Raccoon Creek	12/10/2002	1.04	mg/L	0.17	0.87
Rancocas Creek	6/7/2002	2.56	mg/L	0.42	2.14
Rancocas Creek	7/16/2002	2.29	mg/L	0.37	1.92
Rancocas Creek	10/7/2002	2.13	mg/L	0.35	1.78
Rancocas Creek	12/13/2002	2.41	mg/L	0.39	2.02
Red Clay Creek	7/18/2002	0.63	mg/L	0.10	0.52
Red Clay Creek	8/29/2002	11.10	mg/L	1.81	9.29
Red Clay Creek	12/16/2002	0.43	mg/L	0.07	0.36
Red Clay Creek	12/20/2002	6.18	mg/L	1.01	5.17
Salem Creek	7/16/2002	1.46	mg/L	0.24	1.22
Salem Creek	12/13/2002	2.95	mg/L	0.48	2.47
White Clay Creek	7/18/2002	0.46	mg/L	0.07	0.38
White Clay Creek	8/29/2002	8.94	mg/L	1.46	7.48
White Clay Creek	12/16/2002	0.50	mg/L	0.08	0.41

POC concentrations for unsampled tributaries in Zone 6 were estimated from data reported by the University of Delaware for dry weather concentrations. The mean ratio of wet weather to dry weather POC concentration for all other tributaries was used to estimate a wet weather concentration from the dry weather concentrations reported by the University of Delaware. In addition carbon loads for Assunpink Creek and the Stowe River were estimated as the mean dry weather concentration for all other tributaries in Zones 2 through 5. Wet weather concentrations for the Stowe and Assunpink were estimated by multiplying the estimated dry weather concentration by the mean ratio of wet weather to dry weather POC concentration for all other tributaries.

Based on the analysis of paired POC and chlorophyll-a measurements in the main stem (Section 2.3.2), we observed that our assumed carbon to chlorophyll ratio of 40 resulted in a mean BIC/POC ratio of 0.1633. We assumed that this same relationship would hold true for the tributaries, and estimated BIC and PDC as follows:

$$BIC = 0.1633 \times POC$$

$$PDC = (1 - 0.1633) \times POC$$

2.3.6 Point Discharge Carbon Loads

In order to estimate the carbon load from the point dischargers, we considered two different methods for estimating POC from more routinely monitored effluent parameters (BOD_5 and TSS). For both approaches, we assumed that the point sources discharged no live carbon (i.e. BIC) and hence assigned the entire carbon load from these sources to PDC.

Method 1 is from Appendix B of the EPA report "Progress in Water Quality: An Evaluation of the National Investment in Municipal Wastewater Treatment, EPA-832-R-00-008, June 2000." This method estimates POC as a function of TSS and ratios of organic matter to total solids and carbon to dry weight of organic matter, as shown in the equation below:

$$POC \approx TSS \times \left(\frac{POM}{TSS}\right) \times \left(\frac{C}{DW}\right)$$

where

TSS	=	Total suspended solids
POM	=	Particulate organic matter
C	=	Carbon
DW	=	Dry weight

For municipal wastewater secondary treatment, EPA used values of 0.67 for POM/TSS and 0.44 for C/DW.

Method 2 is a regression developed from paired POC and BOD_5 data from 6 Water Pollution Control Plants in New York City, as part of a water quality modeling effort (Hydroqual 1999). As shown below, the equation estimates POC as a function of BOD_5.

$$POC = 4.68 + 0.31 \times BOD_5$$

To compare these two methods, we computed POC based on reported daily TSS data using Method 1 and reported daily BOD5 data using Method 2. Figures 2.6 and 2.7 show the results for two different waste water treatment facilities during December 2001.

Figure 2.6 - Comparison of 2 Methods for Estimating POC from Reported TSS and BOD_5 Data using Philadelphia SE Plant Data, December 2001

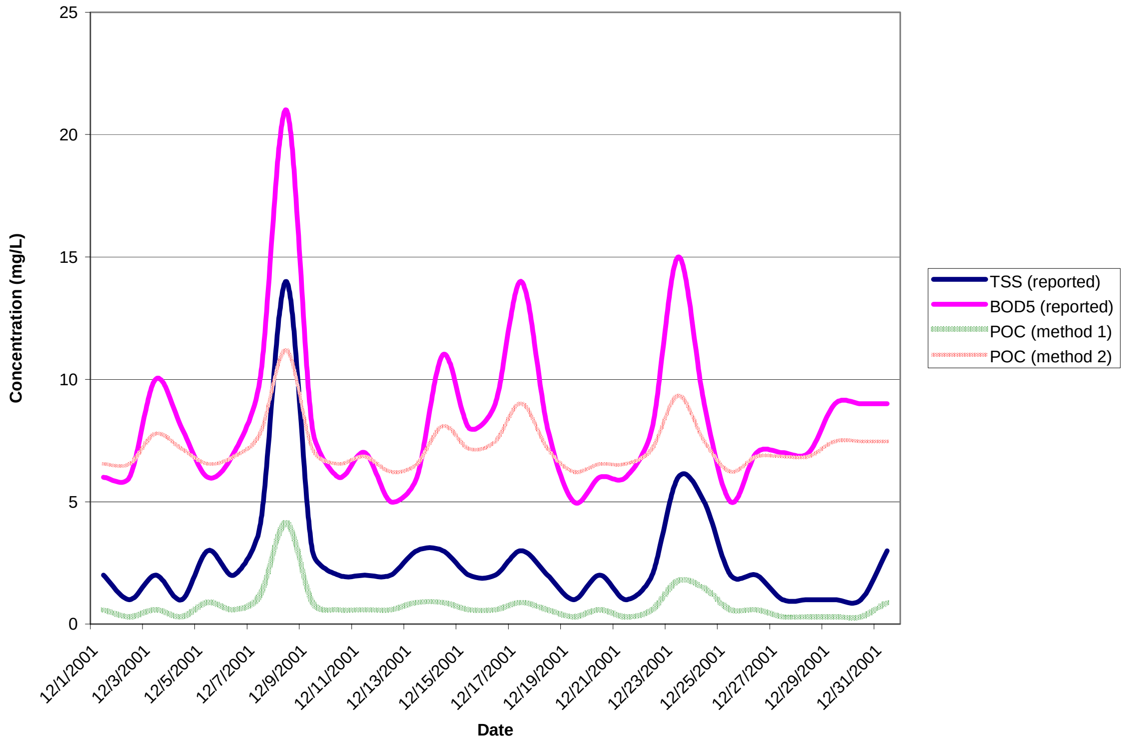
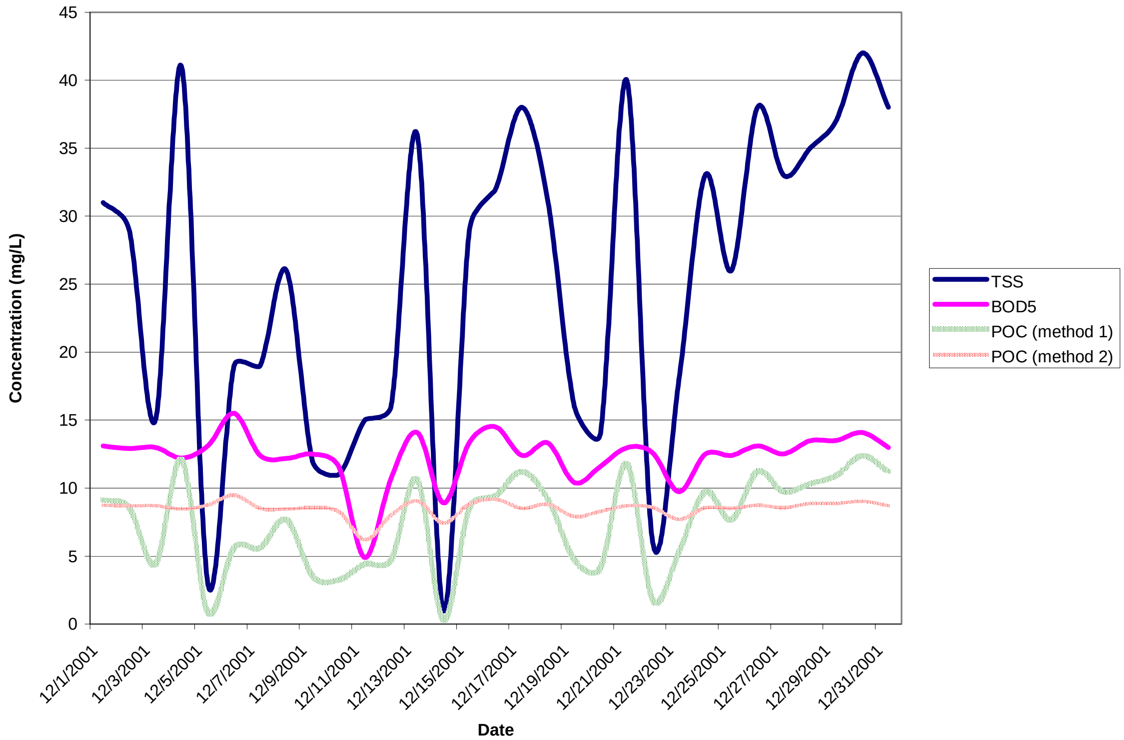


Figure 2.7 - Comparison of 2 Methods for Estimating POC from Reported TSS and BOD5 Data using Morrisville Plant Data, December 2001



Although we would expect TSS to be an upper limit for the potential value of POC, use of Method 2 frequently results in an estimated POC concentration exceeding the reported TSS concentration, as shown in Figures 2.6 and 2.7. Since Method 1 uses TSS to calculate POC, Method 1 estimated POC is always less than TSS.

Figure 2.8 - Comparison of 2 Methods for Estimating POC from BOD_5 and TSS

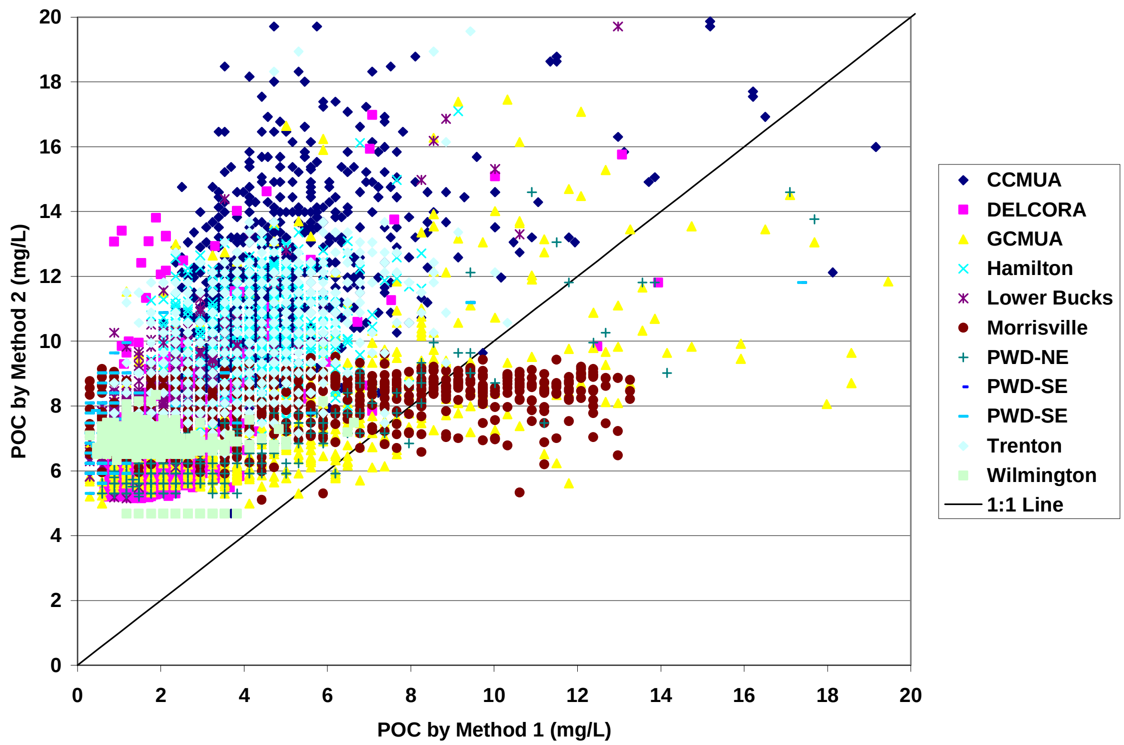


Figure 2.8, comparing POC concentration estimates using the two methods shows that Method 2 generally yields a higher POC concentration estimate than Method 1.

Given the tendency of Method 2 to result in a POC concentration higher than the measured TSS, we recommended to the Expert Panel that Method 1 be used in this iteration. The Expert Panel concurred, and Method 1 was used to estimate POC from daily TSS measurements.

For smaller municipal wastewater treatment facilities that were not required to submit daily measurements, we computed a POC concentration using Method 1 based on a typical TSS effluent concentration of 17.2 mg/L for secondary treatment as reported in *"Appendix B - Progress in Water Quality: An Evaluation of the National Investment in Municipal Wastewater Treatment, EPA-832-R-00-008, June 2000."* This results in a POC concentration of 5.07 mg/L, which is consistent with the computed POC concentrations from daily TSS measurements shown in Figure 2.8.

For facilities discharging primarily stormwater runoff, we estimated a POC concentration based on a mean general urban runoff concentration of 150 mg/L TSS, from the EPA stormwater database as reported in Horner (1994) and an assumed fraction organic carbon of 0.1. Again, we assumed that all particulate carbon from facilities discharging primarily stormwater runoff was PDC rather than BIC. This results in a PDC concentration of 15 mg/L from these facilities.

For facilities discharging primarily industrial process effluent, it is anticipated the carbon concentrations could vary widely from relatively high to undetectable concentrations. For the most part, carbon concentrations are not measured in the industrial process effluent. We presumed that, on average, industrial process effluent should have a lower carbon concentration than municipal wastewater treatment effluent. As a default, we assumed a PDC concentration of 2 mg/L for industrial process water. Since industrial process effluent flow contributes only 13% of the total point discharge flow, compared to nearly 87% contributed by municipal waste water treatment flow, errors associated with this default assumption should be minimized.

2.3.7 Atmospheric Deposition Carbon Loads

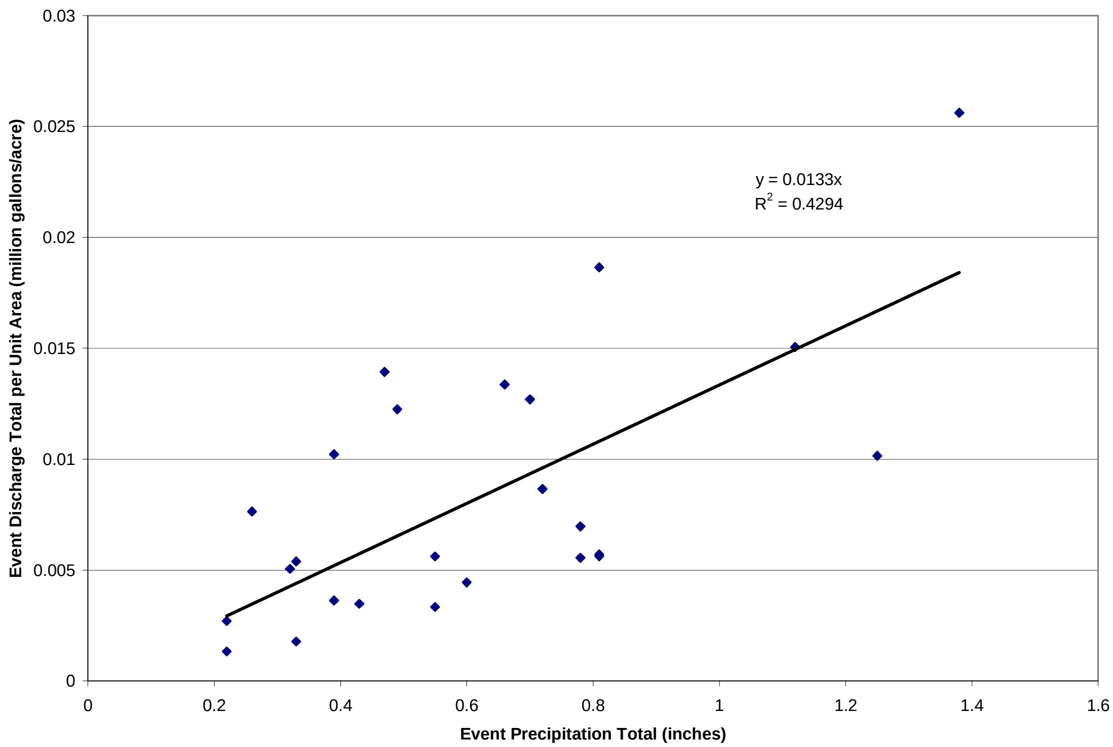
We assumed that all atmospheric particulate carbon was in the form of PDC rather than BIC. We consulted with Rutgers University to estimate the atmospheric deposition of particulate carbon. Based on Rutgers long term atmospheric particulate measurements, we assumed an atmospheric particulate solids concentration of 20 $\mu g/m^3$ with a fraction organic carbon of 0.1 and deposition velocity of 0.75 cm/s for all segments. This resulted in an atmospheric PDC deposition rate of 1.296E-6 kg PDC m^{-2} day^{-1}.

2.3.8 Combined Sewer Overflow Carbon Loads

To estimate PDC load from Combined Sewer Overflows, we multiplied the estimated daily flow and estimated daily PDC concentration. We assumed that all CSO particulate carbon was in the form of PDC, as opposed to BIC.

Philadelphia and DELCORA provided daily flow estimates based on their CSO discharge models. For Wilmington and Camden, we estimated CSO daily flows by regressing measured discharges with measured rainfall during those discharge events, to obtain an estimate of gallons/acre/inch. We extrapolated this estimate to the entire CSO service area and multiplied by the daily 24-hour rainfall totals for each day of the simulation period to estimate daily discharge volume. Figure 2.9 shows this analysis for two Wilmington subbasins.

Figure 2.9 - Lumped Linear Regression of Unit Area Discharge vs. Event Precipitation Totals for the Silverbrook Run and Formans Run Subbasins of the Wilmington CSO Service Area



Philadelphia and DELCORA provided daily TSS and BOD_5 measured treatment plant influent concentrations, as requested by DRBC. Plant influent concentrations are assumed to be comparable to the CSO discharge concentrations during discharge events. Wilmington and Camden declined to provide this data, so the daily values for these facilities were estimated as the mean of the Philadelphia and DELCORA TSS and BOD_5 concentrations for each day during the simulation period. We assumed that all particulate carbon associated with CSO discharges would be in the form of PDC, as opposed to BIC. We estimate the PDC concentration from the reported TSS data using the following equation from EPA (2000).

$$POC \approx TSS \times \left(\frac{POM}{TSS}\right) \times \left(\frac{C}{DW}\right)$$

where

TSS	=	Total suspended solids
POM	=	Particulate organic matter
C	=	Carbon
DW	=	Dry weight

We used the EPA recommended values for raw municipal wastewater of 0.75 for POM/TSS and 0.44 for C/DW.

2.3.9 Non-Point Source Carbon Loads

In order to estimate PDC loads from broad land use associated non-point sources, we modified the framework developed by Camp Dresser McKee (CDM) to estimate PCB loads (Smullen 2003). With the support of the Philadelphia Water Department, CDM developed a non-point source loading framework to estimate daily non-point source loads from the area between the tributary monitoring locations and the mainstem Delaware. CDM originally considered four (4) land use categories for non-point source loads:

- agricultural
- rural/open/ forested
- open water/wet-wetlands, and
- urban/suburban/commercial.

We estimated PDC loads from urban-suburban and rural-rural suburban land use categories. Although CDM had also included an open water category for estimating PCB non-point source loads, this category was not included for estimation of PDC, since atmospheric deposition of PDC onto the water column and marsh generated PDC were estimated explicitly in other categories.

For the urban-suburban land use category, daily PDC loads are estimated from the following:

$$L_i = A_U \times d_r \times C_i$$

where:

L_i = Pollutant Load Estimate from Urban-Suburban Land use areas
A_U = Area of urban land
d_r = rainfall-runoff depth as estimated by a modified rational formula approach
C_i = constant pollutant concentration – [Event Mean Concentration (EMC)]

For C_i, we estimated a POC concentration based on a mean general urban runoff concentration of 150 mg/L TSS, from the EPA stormwater database as reported in Horner (1994), and an assumed fraction organic carbon (f_{oc}) of 0.05. This f_{oc} is lower than the assumed f_{oc} used for industrial stormwater runoff, representing our assumption that localized higher f_{oc}'s associated with spills and accidental releases may be more concentrated at industrial sites and more diffused in the general urban landscape. We assumed that all non-point source derived particulate carbon would be in the form of PDC, rather than BIC.

For the rural/rural-suburban landuse category, we used published estimated area export rates from Horner 1992 as published in Horner 1994. We considered the land uses shown in Table 2.8 as likely components of the rural/rural-suburban category and assumed a value of 300 lbs acre^{-1} year^{-1} to represent a composite rural land use category.

Table 2.10: Median TSS Loading Estimates for Rural subcategories.

Land Use Category	TSS Loading Median Value (lbs/ac/year)
Forest	76.5
Grass	308
Pasture	305

Again, we assumed an f_{oc} of 0.05 and treated all particulate carbon as PDC rather than BIC.

The total daily PDC load from non-point sources, therefore is the sum of the urban-suburban and rural/rural-suburban load. Since the urban-suburban load is a function of precipitation runoff, this value is equal to zero on days without precipitation, and equal to a value proportional to the rainfall total on days with precipitation. By contrast, the rural/rural-suburban load is constant on all days. Thus, the sum of these two loads yields a baseline daily load which is the same on all days without rainfall, that is proportionally increased on days with rainfall.

Finally, the original CDM load framework apportioned loads into each model segment by determining the number of subwatersheds that intersected the model segment boundaries and dividing the total load from those subwatersheds by the number of subwatersheds to approximate the discrete load to the specific segment. Since the model employs segments of varying size, we found that spatially smaller segments tended to receive higher PDC loadings than larger segments, resulting in unrealistically uneven burial rates between larger and smaller segments. To mitigate this effect, we totaled the non-point source PDC loads for each zone and then apportioned them into the specific segments using the relative surface area of each segment in the zone. Thus larger segments would receive proportionally larger loads than smaller segments. As expected, this reduced the unevenness of burial rates between larger and smaller segments.

2.4 penta-PCB Load Estimates

penta-PCB loads were estimated for each day of the 577 day continuous simulation period. Figure 2.10 shows a summary of the 577 day total loads for each source category. Again, the “Boundary” category refers to the Delaware at Trenton and the Schuylkill Rivers, and is not strictly a load. Figure 2.11 shows the load by category for each zone. It should be noted that the Contaminated Site category provides the majority of the load for Zones 3, 4, and 5, while the boundary load, from the Delaware at Trenton, provides most of the load in Zone 2.

Figure 2.10 - 577 Day penta-PCB Load by Source Category

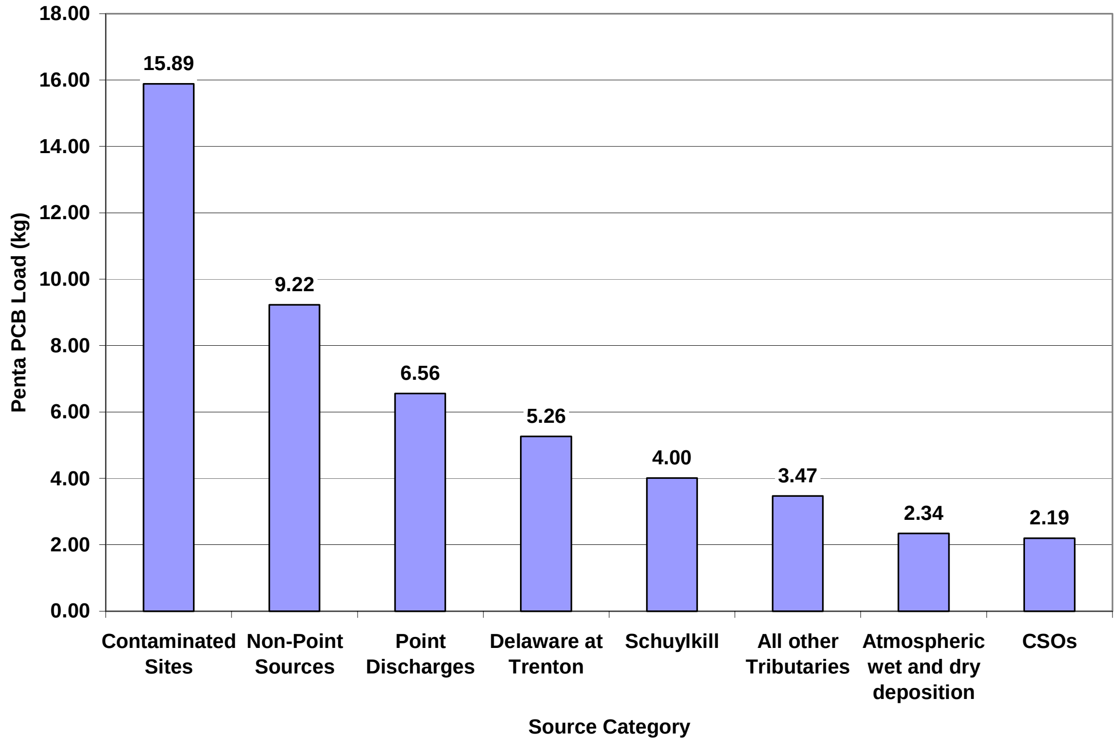
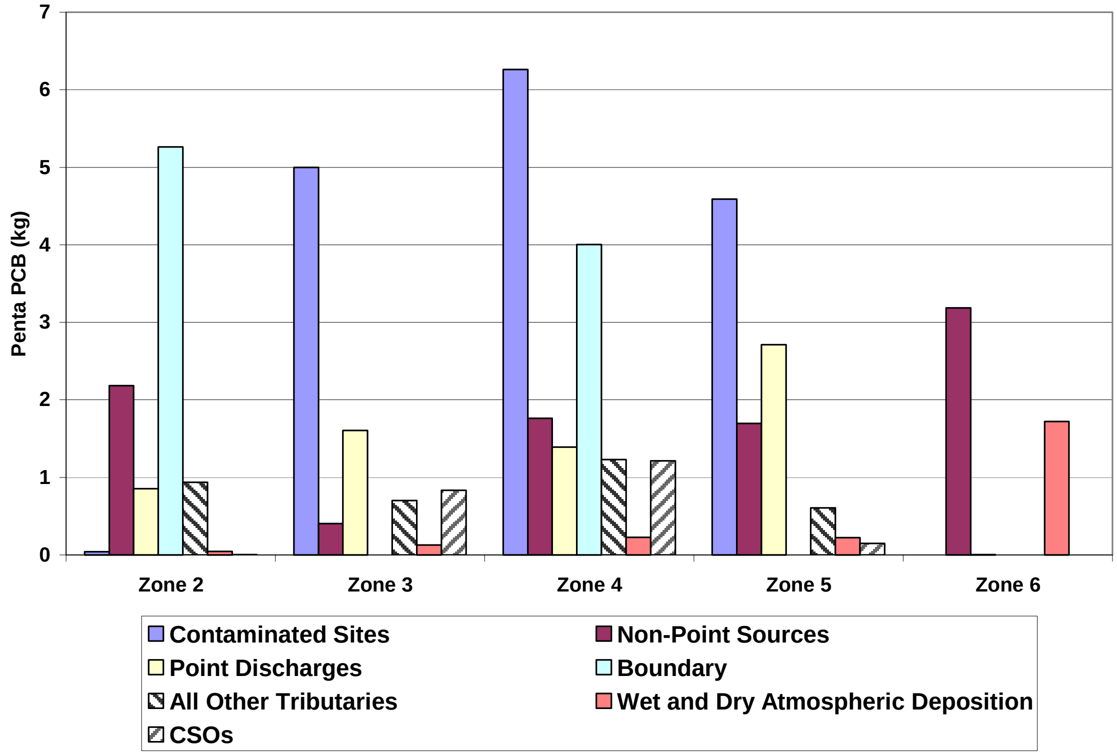


Figure 2.11 - 577 Day penta-PCB Load by Source Category for Each Zone



2.4.2 Contaminated Site penta-PCB Loads

For the contaminated site category, EPA Regions 2 and 3 and the states of Pennsylvania, New Jersey, and Delaware estimated the PCB loads from the contaminated sites under their respective jurisdiction. EPA and states reviewed the sites under their jurisdiction, developed ranking criteria to identify a subset of sites likely to contribute a PCB load to the Delaware Estuary, and developed load estimates for that subset based on site PCB measurements. Only sites located between the tributary monitoring locations and mainstem Delaware were considered. Effects of sites located upstream of tributary monitoring stations are assumed to have been captured as part of the overall tributary load estimates.

In general, the loading methodology involved estimating the solids loss from the various contaminated sites, and multiplying the concentration of PCBs measured in surface soils to estimate the mass of PCBs transported off site. EPA and the states used slightly different approaches to estimating the solids loss. EPA used the universal soil loss equation (USLE) while the states employed area solids yield rates reported by Dunne and Leopold (1978). Both EPA and the states reviewed site files to obtain estimates of surface soil PCB concentrations. In addition, DNREC estimated the contribution of a groundwater discharge pathway for the AMTRAK Former Refueling Facility, based on site groundwater concentration measurements and a calculated Darcy flux. Similarly, DRBC estimated a groundwater pathway load for the Metal Bank site, based on groundwater discharge estimates performed by K.W. Brown (1995) and the partitioning coefficient for combined soil and residual petroleum.

In most cases, PCB concentrations were reported in total PCBs. In order to estimate the proportion of penta-PCB, we multiplied the site specific total PCB concentration by the estimated proportion of penta-PCB produced as part of overall domestic PCB production. Domestic Aroclor production estimates from EPA/600/P-96/001F were combined with congener composition data for Aroclors by Frame (1996) to yield a relative penta proportion of 14.65% of domestic production.

Overall, 49 loads were considered for the contaminated site category, as shown in Table 2.9. It should be noted that the state of New Jersey provided a copy of the EQUIS database for contaminated sites. However, given the absolute deadline for completion of the TMDL, the window of opportunity for incorporating new load estimates closed before NJ site load estimates could be developed.

Table 2.11: Contaminated Site penta-PCB Load Estimates

Facility	Daily penta-PCB Load (kg/day)	Prepared by
Castle Ford - DE-192	1.4374E-06	EPA
Forbes Steel & Wire Corp. - DE-165	5.1989E-06	EPA
Rogers Corner Dump - DE-246	1.0465E-04	EPA
Industrial Products - DE-030	5.1129E-05	EPA
Chicago Bridge and Iron - DE-038	3.2768E-03	EPA
ABM-Wade, 58th Street Dump - PA-0179	1.9739E-06	EPA
O'Donnell Steel Drum - PA-0305	3.4939E-07	EPA
Conrail-Wayne Junction - PA-215	2.3043E-03	EPA
CONRAIL, Morrisville Lagoons - PA-441*	5.4056E-06	EPA
Pennwalt Corp. - Cornwells Heights - PA-0031*	3.1227E-07	EPA

Table 2.11: Contaminated Site penta-PCB Load Estimates (continued)

Facility	Daily penta-PCB Load (kg/day)	Prepared by
Front Street Tanker - PA-2298	1.9914E-06	EPA
8th Street Drum - PA-3272	8.9655E-07	EPA
East 10th Street Site - PA-2869	1.0076E-02	EPA
Metal Bank - PA-2119	9.9092E-05	EPA
Lower Darby Creek Area Site - PA-3424	1.8481E-04	EPA
Roebling Steel Co.	4.9609E-05	EPA
Bridgeport Rental & Oil Services (BROS)	5.8140E-04	EPA
Dana Transport Inc.	3.8523E-08	EPA
Harrison Avenue Landfill	6.2542E-03	EPA
Metal Bank groundwater pathway	9.8312E-07	DRBC
AMTRAK Former Refueling Facility	1.3182E-03	DNREC
Gates Engineering	6.8226E-10	DNREC
AMTRAK Wilmington Railyard	1.6238E-03	DNREC
Diamond State Salvage	0.0000E+00	DNREC
NeCastro Auto Salvage	1.2867E-05	DNREC
Hercules Research Center	4.6121E-06	DNREC
Dravo Ship Yard	5.3216E-05	DNREC
DP&L/Congo Marsh	2.7290E-07	DNREC
American Scrap & Waste	7.4230E-04	DNREC
Pusey & Jones Shipyard	1.6033E-06	DNREC
Delaware Car Company	0.0000E+00	DNREC
Bafundo Roofing	1.5692E-04	DNREC
Kreiger Finger Property	1.5828E-04	DNREC
Clayville Dump	0.0000E+00	DNREC
Electric Hose & Rubber	8.8694E-05	DNREC
Penn Del Metal Recycling	1.1407E-04	DNREC
E. 7th Street North & South	5.7992E-05	DNREC
Delaware Compressed Steel	6.2877E-06	DNREC
Newport City Landfill	0.0000E+00	DNREC
DuPont Louviers – MBNA	9.5516E-08	DNREC
North American Smelting Co.	1.2821E-05	DNREC
RSC Realty	3.4113E-05	DNREC
AMTRAK CNOC	0.0000E+00	DNREC
Wilmington Coal Gas – N	2.2378E-06	DNREC
Del Chapel Place	2.2515E-06	DNREC
Kruse Playground	1.0643E-06	DNREC
Budd Metal	6.3450E-06	DNREC
Fox Point Park Phase II	1.1708E-04	DNREC
BENSALEM REDEV LP ELF ATOCHEM CORNWELL HGT	1.7561E-05	PADEP

2.4.3 Non-Point Source penta-PCB Loads

As with PDC, in order to estimate penta-PCB loads by broad land use associated non-point sources, we used the framework developed by Camp Dresser McKee (CDM) (Smullen 2003). With the support of the Philadelphia Water Department, CDM developed a non-point source loading framework to estimate daily non-point source loads from the area between the tributary monitoring locations and the mainstem Delaware. For constant concentration model and atmospheric deposition/watershed pass-through rate model applications, four (4) land uses were developed:

- agricultural
- rural/open/ forested
- open water/wet-wetlands, and
- urban/suburban/commercial.

The framework estimates PCB loads from urban-suburban, rural-rural suburban, and open water land use categories.

For the urban-suburban land use category, daily penta-PCB loads are estimated from the following:

$$L_i = A_U \times d_r \times C_i$$

where:

L_i = Pollutant Load Estimate from Urban-Suburban Land use areas
A_U = Area of urban land
d_r = rainfall-runoff depth as estimated by a modified rational formula approach
C_i = constant pollutant concentration – [Event Mean Concentration (EMC)]

The EMC is defined as the total mass load of a chemical parameter yielded from a site during a storm divided by the total runoff water volume discharged during the event. For this project the EMC for PCBs was developed through a collaborative literature search performed by Philadelphia Water Department, CDM, and DuPont, with the EMC database being developed and maintained by DuPont.

The literature review team collected and reviewed more than 100 articles and reports dating from 1979 to the present. Articles and reports covered data from over 130 station storms from 70 sites in 20 cities in Canada, the U.S., France, Germany, and Japan. Of the 100+ articles reviewed, 12 yielded useful runoff data. Quantiles of the lognormal EMC from the literature are shown in Table 2.10.

Table 2.12: Quantiles of the Log-Normal Event Mean Concentration

Quantile	Estimate	Units
0.01	2.20	ng/L
0.05	5.85	ng/L
0.25	23.55	ng/L
0.5	61.99	ng/L
0.75	163.20	ng/L
0.95	656.93	ng/L
0.99	1746.90	ng/L

Load estimates were based on the 50^{th} percentile EMC value of 61.99 ng/L. In order to estimate the proportion of penta-PCB, we multiplied the total PCB EMC by the estimated proportion of penta-PCB produced as part of overall domestic PCB production. Domestic Aroclor production estimates from EPA/600/P-96/001F were combined with congener composition data for Aroclors by Frame (1996) to yield a relative penta proportion of 14.65% of domestic production.

For the agricultural, rural/open/ forested, and open water/wet-wetlands land use categories, the framework utilized atmospheric deposition data provided by Rutgers University and an assumed pass-through rate to estimate penta-PCB loads. The framework assumed pass through rates of 10% for agricultural and rural/open/ forested land use categories, and 90% for open water/wet-wetlands. The original framework utilized a single dry deposition rate for the estuary. In order to be consistent with the atmospheric deposition estimates, and to take advantage of more refined atmospheric data, we restructured the framework to use spatially varied dry deposition rates appropriate to each subwatershed.

Finally, the original CDM load framework apportioned loads into each model segment by determining the number of subwatersheds that intersected the model segment boundaries and dividing the total load from those subwatersheds by the number of subwatersheds to approximate the discrete load to the specific segment. Since the model employs segments of varying size, we found that spatially smaller segments tended to receive higher loadings than larger segments, resulting in unrealistically uneven burial rates between larger and smaller segments. To mitigate this effect, we totaled the non-point source loads for each zone and then apportioned them into the specific segments using the relative surface area of each segment in the zone. Thus larger segments would receive proportionally larger loads than smaller segments.

2.4.4 Point Discharge penta-PCB Loads

Daily point discharge penta-PCB loads were estimated by computing the product of daily flows (as described in Section 2.2) and outfall specific mean or measured wet and mean or measured dry weather concentrations, as the sum of penta congeners, toggled by precipitation data. Dry concentrations were used for all days with total rainfall less than

0.1” and wet concentrations were used for all days with total rainfall equal to 0.1” or greater. For continuous discharges with minimal stormwater influence, the wet weather concentration was set equal to the dry weather concentration.

Discharger reported PCB data was used to determine the wet and dry weather concentrations. Congener concentrations were estimated for non-detect data by setting the concentration for that congener at one half of the detection limit. Data flagged with “J”, indicating an estimated value, was used at the estimated value. Coeluting congener concentrations were counted one time only, to avoid artificial inflation of the penta concentration associated with assigning duplicate concentration values for two or more coeluting congeners. Data was not adjusted to account for concentrations measured in field, trip, or rinsate blanks.

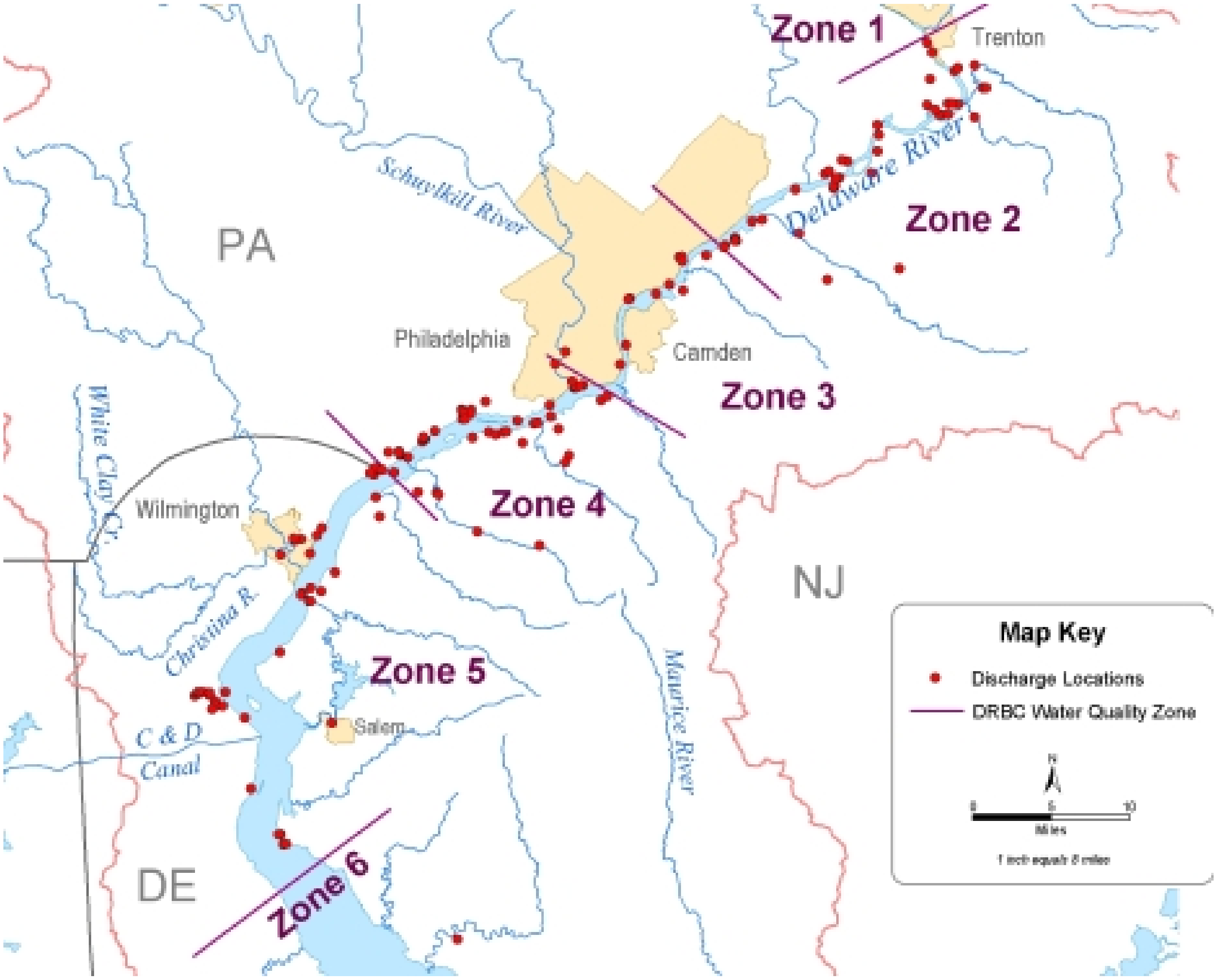
Although sampling was required for non-contact cooling water discharges, estimated loadings from these facilities were not used in this phase of modeling. A review of the influent and effluent concentration data indicated that it was not possible to determine a net load with the limited available data.

Table 2.11 shows the estimated 577 day penta-PCB load for each point discharge in the model in descending order. Discharge ID is a combination of the facility NPDES number and the outfall number or name. Figure 2.12 shows the point discharge the locations.

Table 2.13: Estimated 577 day penta-PCB Load by Point Discharge

Discharge ID	577 Day Penta PCB Load (kg)	Discharge ID	577 Day Penta PCB Load (kg)	Discharge ID	577 Day Penta PCB Load (kg)
DE0000256-101	1.6405E+00	PA0012769-009	1.2039E-02	NJ0004391-003A	4.2689E-04
DE0020320-001	7.4880E-01	NJ0024449-001	1.1099E-02	PA0045021-001	3.7258E-04
PA0026689-001	7.1471E-01	NJ0027481-001	1.0899E-02	PA0013323-003	3.5658E-04
PA0026671-001	5.8881E-01	PA0057479-DD3	1.0296E-02	PA0013716-005	3.4763E-04
NJ0026182-001	4.7225E-01	NJ0023701-001	9.0487E-03	PA0012637-007	2.9499E-04
PA0026662-001	3.7951E-01	PA0028380-001	8.9147E-03	DE0021539-001	2.8078E-04
PA0027103-001	1.7854E-01	NJ0004286-001A	8.6842E-03	PA0013323-007	2.1883E-04
NJ0020923-001	1.4056E-01	NJ0004995-441C	7.2394E-03	NJ0005584-002A	2.0318E-04
NJ0026301-001	1.2740E-01	NJ0005045-001	7.0556E-03	NJ0004375-001A	1.9012E-04
NJ0005029-001A	9.9736E-02	NJ0027545-001	6.9896E-03	NJ0005363-017	1.6299E-04
PA0013323-002	8.8458E-02	NJ0030333-001	6.9876E-03	DE0050911-002	1.5168E-04
NJ0005100-001	7.9901E-02	NJ0021601-001	5.9230E-03	PA0013323-016	1.3569E-04
PA0026468-001	7.4536E-02	NJ0033022-001A	5.9191E-03	NJ0005185-002A	1.1314E-04
NJ0004219-001A	7.2746E-02	NJ0024856-001	5.8058E-03	DE0000051-004	9.8613E-05
NJ0022519-001	7.1610E-02	NJ0004278-001A	5.7937E-03	NJ0064696-001A	9.0635E-05
NJ0023361-001	7.1197E-02	PA0051713-001	5.2291E-03	DE0050601-016	8.5350E-05
NJ0024686-001	6.5488E-02	NJ0005240-001A	4.2929E-03	PA0013081-029	7.4575E-05
NJ0005100-662	5.9347E-02	NJ0005584-003A	4.0422E-03	PA0013716-001	7.2527E-05
PA0011533-015	5.7219E-02	NJ0020532-001	3.5158E-03	PA0012637-008	6.3916E-05
DE0020001-001	4.6842E-02	PA0012777-003	2.8323E-03	PA0057690-019	5.7861E-05
PA0013463-002	4.6443E-02	DE0000612-001	2.8184E-03	PA0057690-021	5.7861E-05
PA0012629-002	4.3794E-02	PA0013463-203	2.5395E-03	NJ0033022-002	5.2926E-05
DE0000051-001	3.9050E-02	DE0050911-001	2.4697E-03	NJ0033952-001A	5.0389E-05
NJ0025178-001A	3.8909E-02	NJ0005134-001A	2.3775E-03	NJ0004332-001B	4.0366E-05
PA0026701-001	3.7832E-02	DE0021555-001	2.3568E-03	NJ0005363-005	3.1131E-05
NJ0021598-001	3.6554E-02	NJ0021610-001	2.2231E-03	PA0011622-001	2.9746E-05
NJ0005401-001A	3.1947E-02	NJ0005240-002A	2.0267E-03	NJ0025411-462A	2.1178E-05
NJ0024015-001	3.1680E-02	NJ0022021-001	1.9017E-03	PA0013323-008	2.0217E-05
PA0057479-DD2	2.8296E-02	DE0000647-001	1.3074E-03	PA0012637-006	1.6974E-05
PA0012637-201	2.8031E-02	NJ0025411-461C	1.2856E-03	DE0050601-034	1.3333E-05
NJ0024660-002	2.6736E-02	NJ0004219-007	1.2670E-03	PA0011622-004	1.1400E-05
PA0012777-001	2.2064E-02	DE0020001-003	1.2556E-03	NJ0131342-001A	7.0549E-06
NJ0023507-001	2.1591E-02	DE0050962-003	1.1873E-03	PA0012777-007	6.7437E-06
DE0050962-004	2.0243E-02	NJ0005002-WTPA	1.1368E-03	NJ0005363-006	6.6812E-06
NJ0021709-001	2.0138E-02	NJ0005185-001A	1.0694E-03	NJ0000008-003	6.4344E-06
PA0026450-001	2.0040E-02	DE0020001-002	9.8862E-04	DE0000558-041	6.4309E-06
PA0013323-001	1.7109E-02	NJ0000008-001A	9.7524E-04	NJ0004391-002A	4.8856E-06
PA0027294-001	1.6954E-02	NJ0035394-003A	9.3212E-04	NJ0005401-003A	3.7411E-06
NJ0024007-001	1.6145E-02	NJ0005622-489	9.2285E-04	PA0057690-047	2.7909E-06
NJ0024678-001	1.5170E-02	NJ0004669-001A	8.8145E-04	DE0050601-033	2.6884E-06
NJ0024023-001	1.3390E-02	PA0011622-002	8.4941E-04	NJ0005100-011	2.1883E-06
PA0013463-103	1.3161E-02	PA0043818-001	6.8206E-04	NJ0004332-002A	9.0978E-09
PA0057690-012	1.3045E-02	NJ0005266-002A	4.6582E-04		

Figure 2.12 - Locations of Point Discharges in the Delaware Estuary



2.4.5 Tributary penta-PCB Loads

Tributary penta-PCB loads were estimated by computing the product of gaged or extrapolated daily flows at the monitoring location (as described in Section 2.2.4) and tributary specific mean wet and mean dry weather concentrations, toggled by precipitation data. In all, loads from 20 tributaries (not including the Delaware River at Trenton and the Schuylkill River, which are discussed in Section 2.5) were explicitly computed. The loads from tributaries in Zone 6 were estimated as part of the non-point source load category, by using the entire drainage area to the edge of the Delaware as the non-point source drainage area.

Table 2.14: Estimated 577 Day penta-PCB Load by Tributary

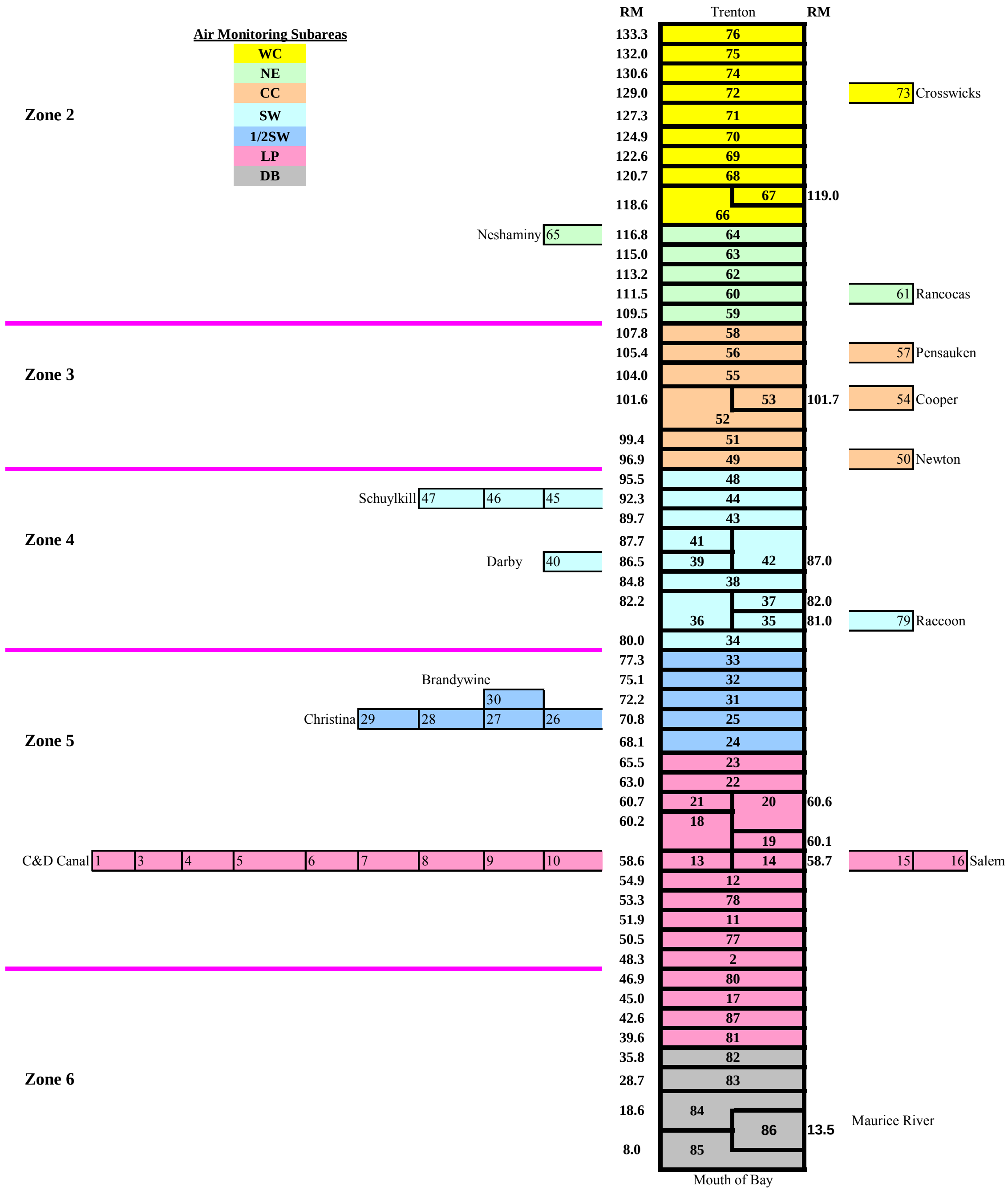
Tributary	577 Day penta-PCB Load (kg)	Tributary	577 Day penta-PCB Load (kg)
Darby	0.56	Alloways	0.12
Assunpink	0.38	Chester	0.11
Mantua	0.35	Red Clay	0.11
Cooper	0.30	Salem	0.11
Rancocas	0.23	Pennypack	0.07
Pennsauken	0.20	Christina	0.07
Frankford	0.20	Raccoon	0.06
Crosswicks	0.18	Brandywine	0.05
Big Timber	0.15	Neshaminy	0.05
White Clay	0.15	Poquessing	0.04

Although 60 tributary penta-PCB samples were collected during the calibration period, 37 results were released by the analytical laboratory in time for use in this iteration of the PCB TMDL. The remaining 23 results are still in process. As such, some tributary wet and dry weather concentrations are estimated. Specifically, the dry weather concentration for Assunpink is estimated from the mean concentration of all other tributaries, and the wet weather concentrations for Darby, Chester, Pennsauken, Cooper, Alloways, Salem, and Assunpink are estimated by multiplying their dry weather concentrations by the mean ratio of wet weather to dry weather concentration for all other tributaries. Tributary sampling is ongoing, and numerous samples have been collected after the end of the calibration period. Therefore, as more data is released by the laboratory, we anticipate refinement of the tributary loads in future phases of work.

2.4.6 Atmospheric Deposition penta-PCB Loads

Wet and dry atmospheric deposition was estimated using data provided by Dr. Lisa Totten of Rutgers University. Dr. Totten oversaw collection of atmospheric particulate and gas phase concentrations of PCB congeners at 6 stations over 30 sampling events between November 2001 and January 2003. Based on preliminary results, Dr. Totten estimated seasonal dry deposition rates and volume weighted rainfall concentrations for 7 subareas. The model segment assignments to specific air monitoring subareas are shown in Figure 2.13. Seasonal penta-PCB dry deposition rates and penta-PCB volume weighted mean rain concentrations are shown in Table 2.13.

Figure 2.13 - Assignment of Air Monitoring Subarea Values to Model Segments



As the remainder of the samples are analyzed, revised atmospheric deposition rates may be incorporated into future phases of work.

Table 2.15: penta-PCB Dry Deposition Rates and Rain Concentrations by Subarea

Subarea	Summer Dry deposition ($ng/m^2/d$)	Fall dry deposition ($ng/m^2/d$)	Winter dry deposition ($ng/m^2/d$)	Spring dry deposition ($ng/m^2/d$)	Volume weighted Concentration in rain (ng/L)
WC	0.26	0.79	0.74	0.63	0.11
NE	3.40	3.40	2.72	5.86	0.66
CC	10.22	6.70	16.20	7.71	0.66
SW	6.60	6.60	6.21	7.14	1.28
1/2SW	3.30	3.30	3.10	3.57	0.64
LP	1.05	1.05	1.05	1.05	0.20
DB	1.27	1.29	1.32	0.88	0.22

Dry deposition was applied on all days, regardless of rainfall. On days with rainfall, the total deposition is equal to the dry deposition applied on all days plus the wet deposition, as the product of the rainfall 24-hour total, segment area, and rain concentration.

2.4.7 Combined Sewer Overflow penta-PCB Loads

Combined Sewer Overflow (CSO) loads were estimated by computing the product of daily CSO flows, as discussed in Section 2.3.8, and treatment plant specific mean wet weather influent concentrations measured in 1996 (DRBC 1998). We assumed that concentration at the plant influent would be comparable to the expected concentrations at the CSO outfalls overall, although individual outfalls may be subject to localized influences in the collection system.

During influent sampling, the Philadelphia Southeast plant was impacted by a spill event, so the concentration value for that facility was estimated using the mean penta-PCB concentration of the other five treatment plants with CSO systems (Philadelphia Northeast and Southwest, DELCOR, Wilmington, and Camden). Similarly, the Philadelphia Southwest plant received return water from sludge handling operations also impacted by the spill, in one of the two influent lines entering the plant. Only the penta-PCB concentration from the non-impacted influent line was used to estimate the Philadelphia Southwest CSO load.

2.5 Boundary Concentrations

Concentrations rather than loads are specified at model boundaries.

2.5.1 Delaware at Trenton

To estimate POC concentrations at the Delaware River at Trenton, we compared 71 paired flow and POC measurements collected by USGS between 1991 and 2001 (USGS 2003). We evaluated numerous approaches for relating POC concentration to flow, including 3 simple linear regressions (Figure 2.14), 3 stratified regressions using a median concentration for lower flows and linear regression of POC and flow for higher flows (Figure 2.15), a 2-tiered step function with a low flow median and high flow median, and the 7-regressor version of the Minimum Variance Unbiased Estimator (MVUE) (Cohn 1989, Gilroy 1990, Cohn 1992) as implemented in the software program ESTIMATOR 2000 (Cohn 2000) using both full and partial data sets. Predicted POC concentrations were plotted against observed POC, as shown in Figure 2.16, to determine which method provided the best prediction of observed POC from measured flow. In addition, we compared estuary POC measurements at the first station below the head of tide, to the concentrations predicted by selected methods. A simple linear regression, with one assumed outlier at the very high flow (~70,000 CFS) excluded, consistently yielded predictions that most closely matched both the 1991-2001 period of record, the calibration period data set at the head of tide, and the observed estuary data at the first station below the head of tide. This regression was therefore used to compute the daily POC concentration for the Delaware River at Trenton for each day of the continuous simulation period, using the measured flow for that day.

Figure 2.14 - Three Linear Regressions of POC versus Flow for the Delaware River at Trenton

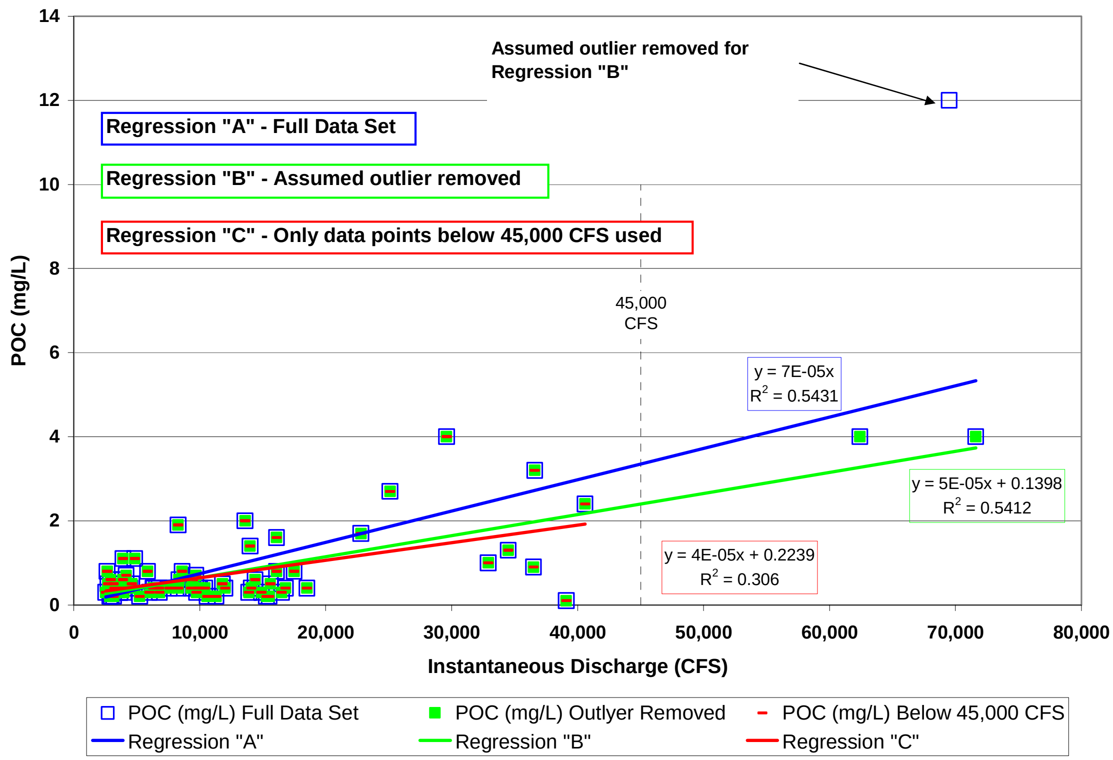


Figure 2.15 - Stratified Relationships of POC versus Flow for the Delaware River at Trenton

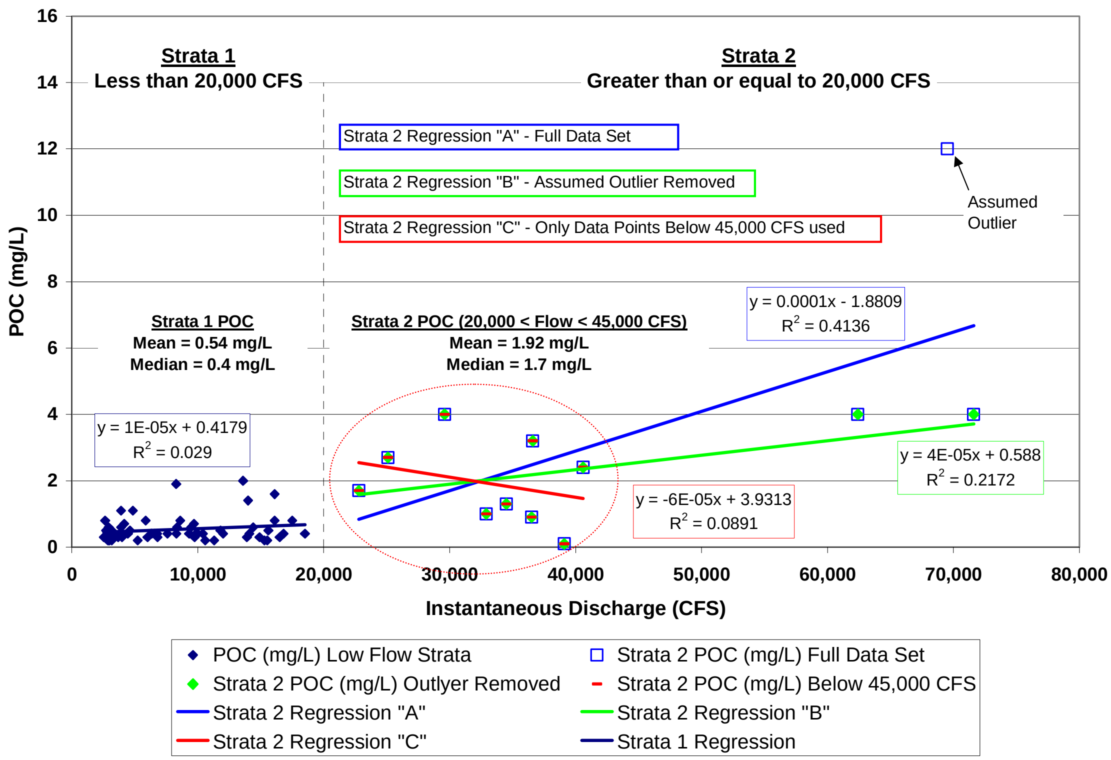
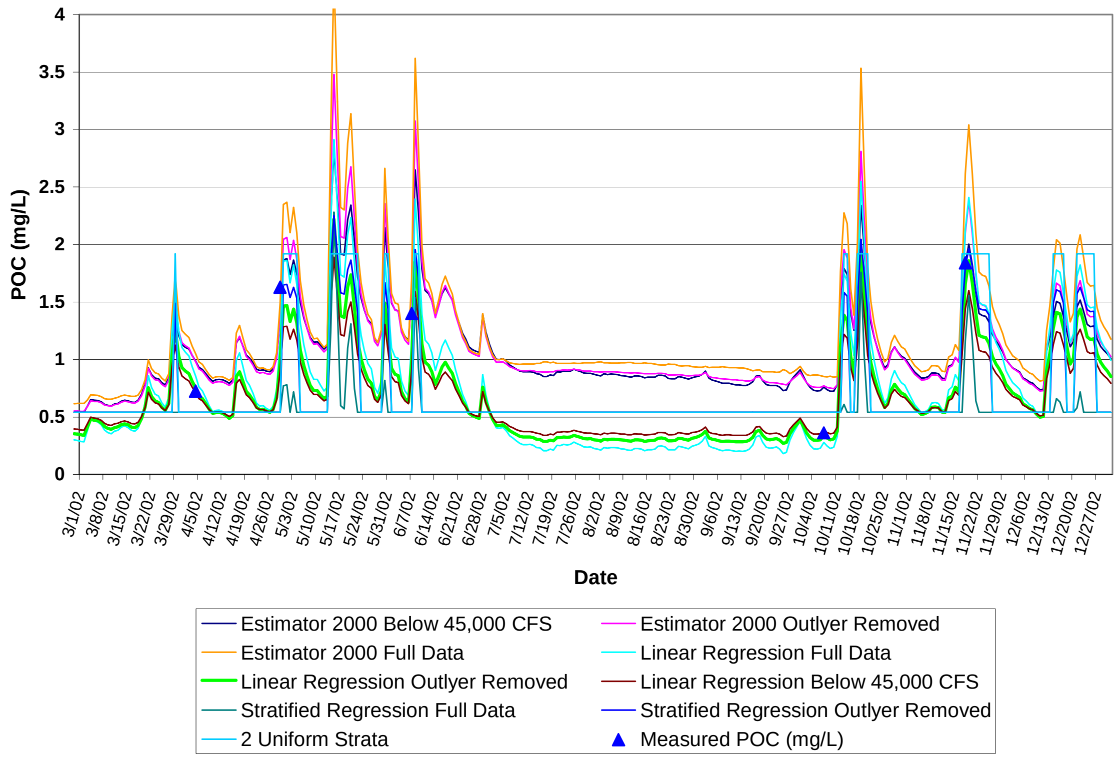


Figure 2.16 - Comparison of Predicted POC concentrations using 9 different methods to observed POC concentrations from the Delaware at Trenton



Based on the analysis of paired POC and chlorophyll-a measurements in the main stem (Section 2.3.2), we observed that our assumed carbon to chlorophyll ratio of 40 resulted in a mean BIC/POC ratio of 0.1633. We assumed that this same relationship would hold true for the Delaware River at Trenton, and subdivided POC into BIC and PDC as follows:

$$BIC = 0.1633 \times POC$$

$$PDC = (1 - 0.1633) \times POC$$

For penta-PCBs, dry and wet weather penta-PCB concentrations for the Delaware River at Trenton were estimated from samples collected in 2000 by USGS and in 2002 by USGS for DRBC. Results from 3 samples collected on a rising hydrograph during wet weather and 2 samples collected during dry weather were available for estimation of mean wet weather and dry weather concentrations. Dissolved and particulate PCBs were measured in the samples collected for DRBC. These fractions were summed to yield a whole matrix PCB concentration, similar to the results provided by USGS under the NAWQA program. Since the USGS data collected under the NAWQA program incorporated higher detection limits than are currently available using method 1668A, concentrations of non-detected congeners were estimated by assigning a congener concentration equal to ½ the detection limit. From these results we specified a wet weather and dry weather concentration on a daily basis for the Delaware River at Trenton. For days with a 24-hour rainfall total less than 0.1”, the dry weather concentration was specified. For days with 24-hour rainfall total of 0.1” or more, the wet weather concentration was specified.

Sample collection at the Delaware River model boundary is ongoing. A larger data set will be available for specifying boundary concentrations in future phases of work.

2.5.2 Schuylkill

To estimate POC concentrations in the Schuylkill River at head of tide, we compared 28 sample records including concurrently collected flow, POC, and TSS measurements. Measurements were collected as part of several different studies by USGS, the Academy of Natural Sciences, and DRBC. Some additional data values consisting of paired flow and TSS and paired flow and POC measurements were also considered. Given the limited paired POC and flow data, and the variability of the POC measurements, we also evaluated regressions of TSS to flow, with secondary regressions of POC to TSS. Ultimately we considered numerous methods for relating POC to flow, including (**A**) linear regression of POC to TSS and linear regression of TSS to flow, (**B**) a 2-tiered step function with a POC concentration of 0.58 mg/L at flows < 10,000 CFS and 24.9 mg/L at flows ≥ 10,000 CFS, (**C**) an exponential regression of POC to flow, (**D**) POC as a function of flow from the 7-regressor version of the Minimum Variance Unbiased Estimator (MVUE) (Cohn 1989, Gilroy 1990, Cohn 1992) as implemented in ESTIMATOR 2000 (Cohn 2000), and (**E**) a linear regression of POC to flow for flows < 10,000 CFS. Other relationships including linear regression of POC from flow for the full flow regime and linear regression of POC to TSS with a 2-tiered TSS step function were considered initially, but failed to demonstrate a reasonable relationship between POC and flow. Again, predicted POC concentrations were plotted against observed POC, as shown in Figures 2.17 and 2.18, to determine which method provided the best prediction of observed POC from measured flow. Since most of the POC observations were grouped at low concentrations, with 1 observation at a high concentration, no method demonstrated an especially strong and reasonable relationship between POC and flow. Ultimately we selected a linear regression of TSS from flow for the full flow regime with a secondary regression of POC from TSS (**Line “A”**). This method tracks the observed relationships between POC and TSS and between TSS and flow, and provides some sense of increasing POC with increasing flow without the artificiality of the step functions. This relationship should be revisited as a more comprehensive database is assembled.

Figure 2.17 - Comparison of Predicted POC concentrations using 5 different methods to observed POC concentrations from the Schuylkill River

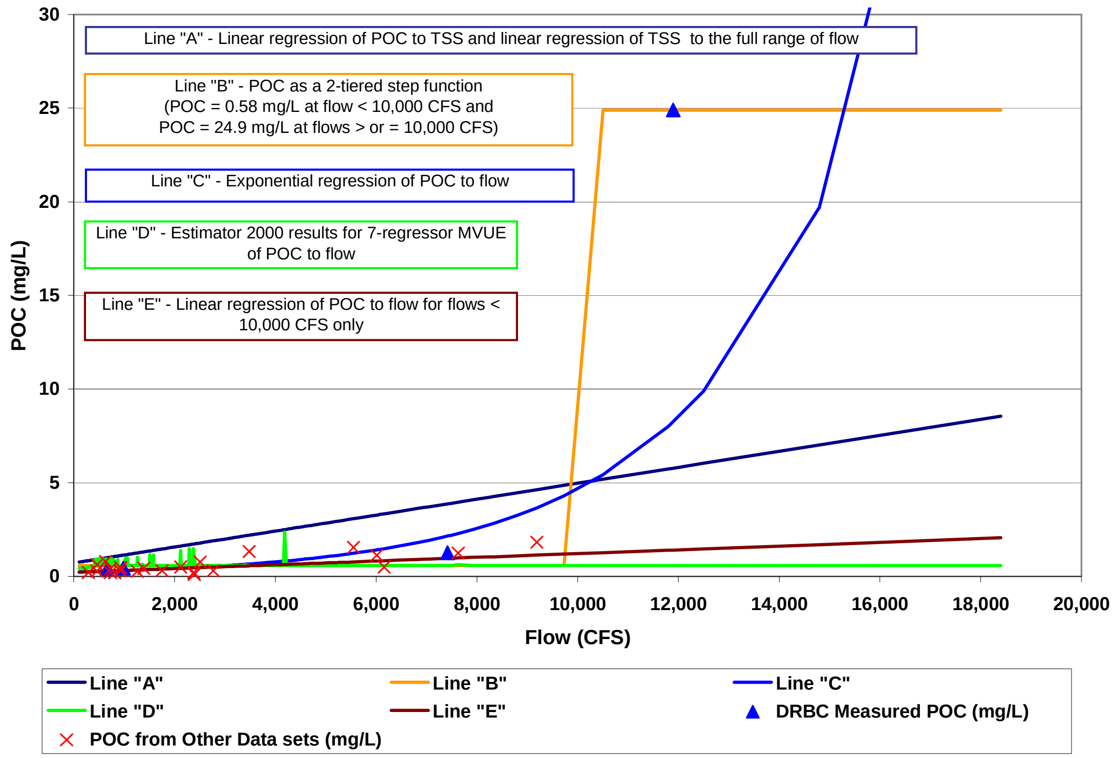
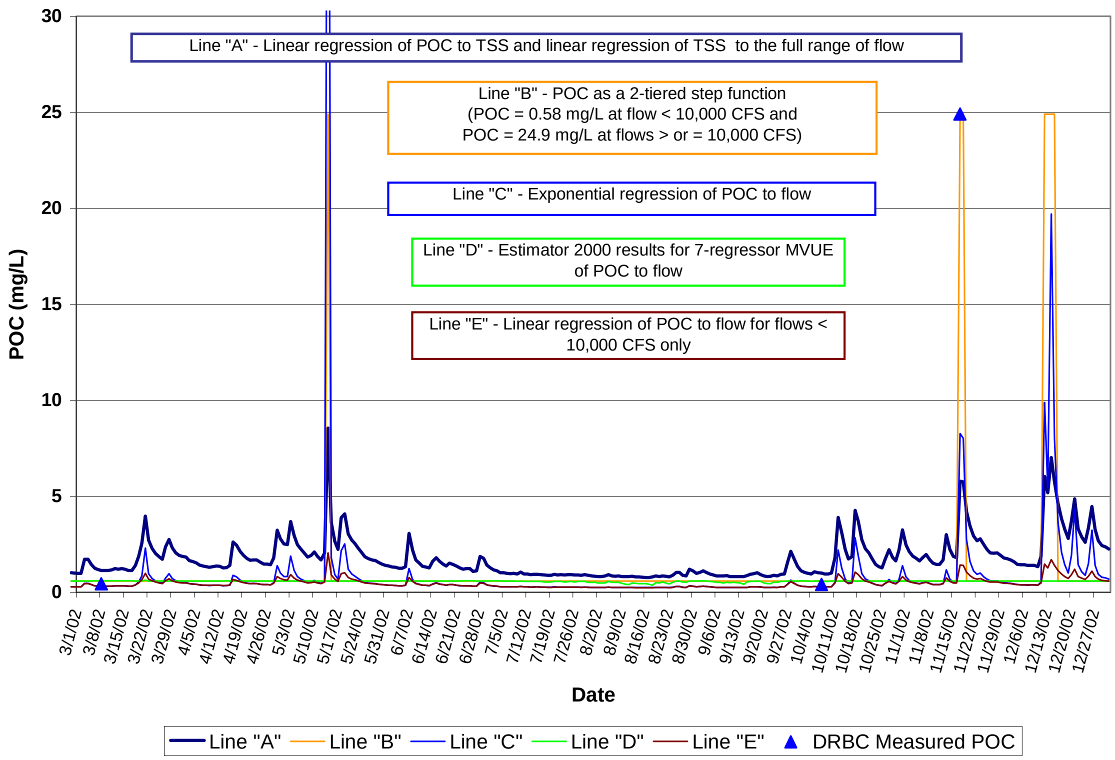


Figure 2.18 - Daily estimated POC concentrations using 5 different methods and Observed POC data from the Schuylkill River



Again, POC was subdivided into BIC and PDC fractions using the method described in the previous section.

For penta-PCBs, dry and wet weather penta-PCB concentrations for the Schuylkill River were estimated from samples collected in 2000 (by USGS) and in 2002 (by USGS for DRBC). Results from 3 samples collected on a rising hydrograph during wet weather and 3 samples collected during dry weather were available for estimation of mean wet weather and dry weather concentrations. Dissolved and particulate PCBs were measured in the samples collected for DRBC. These fractions were summed to yield a whole matrix PCB concentration, similar to the results provided by USGS under the NAWQA program. Since the USGS data collected under the NAWQA program incorporated higher detection limits than are currently available using method 1668A, concentrations of non-detected congeners were estimated by assigning a congener concentration equal to ½ the detection limit. From these results we specified a wet weather and dry weather concentration on a daily basis for the Schuylkill River. For days with a 24-hour rainfall total less than 0.1", the dry weather concentration was specified. For days with 24-hour rainfall total of 0.1" or more, the wet weather concentration was specified.

Sample collection at the Schuylkill River model boundary is ongoing. A larger data set will be available for specifying boundary concentrations in future phases of work.

2.5.3 C&D Canal

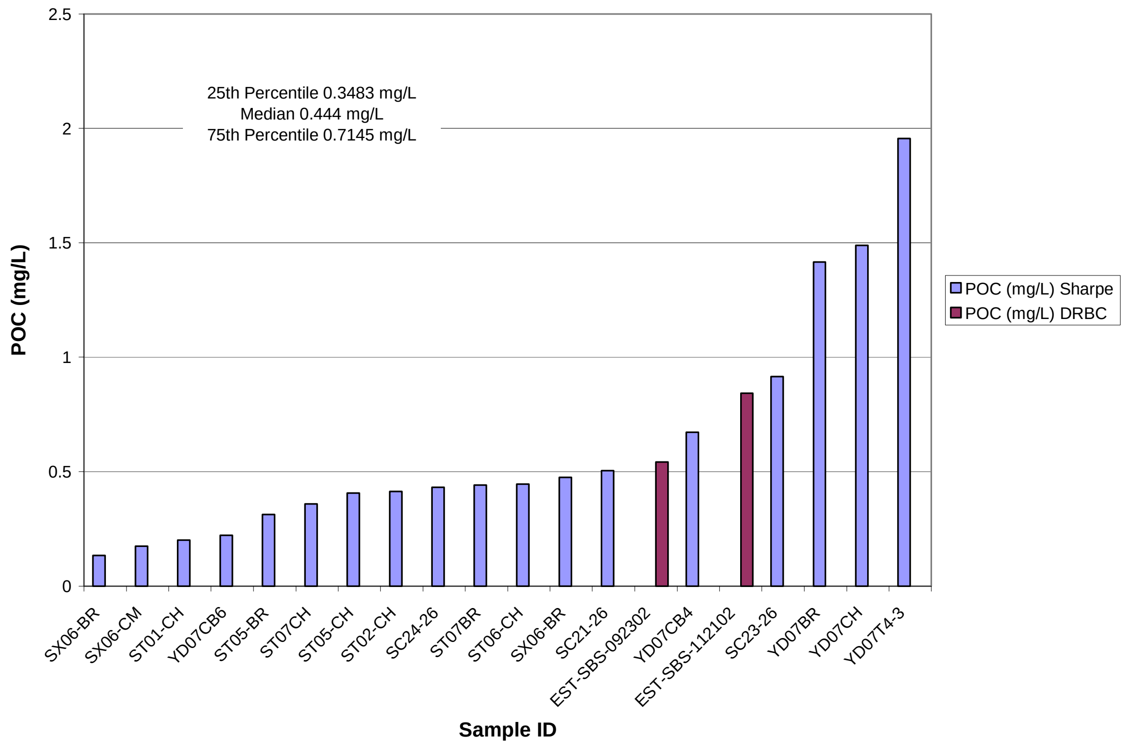
The State of Delaware had collected TOC and DOC measurements at 3 stations within the C&D canal. Although POC can be estimated as the difference between TOC and DOC, in many cases DOC was greater than or equal to TOC in the Delaware C&D Canal data set, potentially resulting from concentrations near the lower quantitation limit for the analytical methods used. Alternatively, we specified the C&D canal concentration at 3.135 mg/L for all simulation days, which was the mean of two measurements collected by DRBC within the canal. More attention should be focused on characterizing the C&D canal concentrations in future phases of work. POC was subdivided into BIC and PDC as discussed in previous sections.

A constant penta-PCB concentration of 902 pg/L was specified for the C&D tidal boundary segment for all simulation days. This value is equal the penta-PCB concentration measured on March 19, 2003, as the sum of particulate and dissolved fractions. This value is also within the range of the autumn and spring median penta-PCB concentrations of 606 to 948 pg/L calculated from measured channel catfish concentrations in the C&D canal.

2.5.4 Ocean Boundary

To estimate the ocean boundary POC concentration, we identified 20 POC measurements from 2 different data sets collected near the mouth of Delaware Bay, as shown in Figure 2.19. The majority of the data was collected by Dr. Jonathan Sharpe of the University of Delaware, with 2 samples collected by DRBC. Results showed a median concentration of 0.44 mg/L. The boundary concentration was therefore set at 0.44 mg/L POC for all simulation days, with individual BIC and PDC fractions being estimated as discussed in the previous sections.

Figure 2.19 - POC measurements from the mouth of Delaware Bay



A constant penta-PCB concentration of 200 pg/L was specified for the ocean boundary for all simulation days. This value is consistent with median and mean concentrations of 199.8 and 208.7 calculated from the NOAA mussel watch data for oysters in lower Delaware bay (NOAA, 1989 and 2003). In estimating this boundary concentration, we investigated available data and found a range of possible concentrations from 97.5 pg/L calculated from mussel tissue data, to 512 pg/L measured in the Lower Harbor Trawl portion of the New York Bight (Litten, 1999). Similarly, our own lower bay measurements ranged from slightly less than 100 to slightly greater than 500 pg/L penta-PCB, with the majority of the measurements near 200 pg/L.

2.6 Physical Parameters: Temperature, Wind Speed, Precipitation

Water and air temperature and wind speed are included in the water quality model and are used to calculate Henry law constants for PCBs. Additionally, precipitation data from three precipitation gaging stations were used to generate discharge flows for dischargers with stormwater outfalls.

2.6.1 Water Temperature

Water temperature values were obtained from three water quality monitoring stations on the Delaware River/Estuary operated cooperatively by the DRBC and the USGS, for the calibration period September 1 2001 through March 31, 2003 at the following stations:

1. 01467200 located at the Ben Franklin Bridge
2. 01477050 located at Chester
3. 01482800 located at Reedy Island

2.6.2 Air Temperature and Wind Speed

Air Temperature and wind speed values from the Philadelphia International airport station was used for the calibration period and were obtained from the National Weather Service web site (http://weather.noaa.gov/).

2.6.3 Precipitation

Precipitation data (24-hour precipitation totals) were obtained from three sites in the Delaware Estuary. Two sites are maintained by National Climatic Data Center and the third site is maintained by the Franklin Institute. Data is available from their respective web sites (http://www.fi.edu/weather/data/, and http://weather.noaa.gov/) and the stations are located at:

1. Franklin Institute, Philadelphia, Pa
2. Neshaminy Falls, Bucks County, Pa
3. Wilmington, New Castle County, De

2.7 Load Uncertainty Analysis

In order to assess the uncertainty associated with the load estimation calculations for each source category, a Monte Carlo analysis was performed for each of the PCB source categories and for the 2 largest carbon source categories. Objectives of this analysis included:

- Estimating the uncertainty for each source category;
- Comparing the uncertainty of various categories;
- Identify reasonable upper and lower loading limits for each source category and for the overall penta-PCB load.

Load estimates were calculated for each segment-day for each source category using an electronic spreadsheet. The Monte Carlo analysis was performed by assigning a probability distribution to each of the elements in the computation. The load estimate for each source category was then iteratively re-computed using different values for each computational element, selected in accordance with the probability distribution for that element, with the results of each iterative computation retained to develop a range and distribution of computed values.

For each source category, numerous assumptions were required in order to specify probability distributions. Figure 2.20 shows a typical point discharge penta-PCB concentration probability distribution. For concentration probability distributions, the assumptions selected depended on how many data points were available for a specific source and which analytical method was used. In general the following rules, in order of preference, were used for specification of a concentration probability distribution:

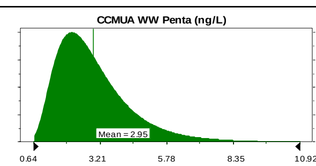
- If analytical method 1668A or 8082A was used and there was sufficient data to calculate a mean and standard deviation (at least 3 data points), a normal distribution was developed to ensure that all concentration values within the distribution were positive (i.e. no negative values). If a normal distribution resulted in negative values, a lognormal distribution was used, with the same source specific mean and standard deviation.
- If analytical method 1668A or 8082A was used, but there were insufficient data points to compute a standard deviation, a lognormal distribution was specified assuming a standard deviation = 0.6 x mean.
- If an Aroclor analytical method was used (contaminated sites and non-point sources only) and mean or a single value was reported, a lognormal distribution was specified assuming a standard deviation = mean.
- If an Aroclor analytical method was used and only a maximum concentration was reported (applies only to a limited number of contaminated sites), a lognormal distribution was specified assuming a standard deviation = mean = ¼ max concentration.
- Finally, if a maximum and mean were reported that could not reasonably be fit to a lognormal distribution, a triangular distribution was specified with the triangle apex (likeliest value) corresponding to the mean reported value and two edges of the triangle corresponding to the maximum and minimum (or zero) reported values. This approach applies only to a very limited number of contaminated sites.

Figure 2.20 - Typical Outfall Specific Lognormal penta-PCB Concentration Probability Distribution.

Lognormal distribution with parameters:

Mean	2.95
Standard Dev.	1.48

Selected range is from 0.00 to +Infinity

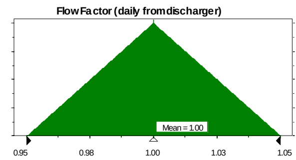


For flow values, a triangular distribution was typically employed, with the reported flow corresponding to the likeliest value (the triangle apex) and some expression of uncertainty defining the upper and lower value limits (right and left hand side) of the triangle, as shown in Figures 2.21 and 2.22.

Figure 2.21 - Flow Factor Probability Distribution applied to Outfall Daily Flow Measurements Provided by the Discharger

Triangular distribution with parameters:	
Minimum	0.95
Likeliest	1.00
Maximum	1.05

Selected range is from 0.95 to 1.05

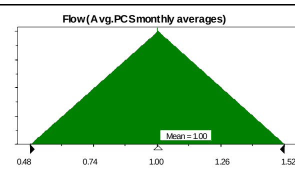


The range of the flow factor applied to daily flow estimated from mean flows reported in PCS was determined by comparing minimum and maximum flows to the mean reported flow, for data sets with both.

Figure 2.22 - Flow factor distribution applied to daily flow estimated from mean flows reported in PCS.

Triangular distribution with parameters:	
Minimum	0.48
Likeliest	1.00
Maximum	1.52

Selected range is from 0.48 to 1.52



Similar expressions of uncertainty were applied to other flow categories as well. For outfalls discharging primarily rainfall runoff, an uncertainty factor with a triangular distribution was applied to the drainage area reported by the discharger, with the reported drainage area set as the likeliest value and the right and left edges of the triangle corresponding to ±10% of that value. The reported curve number was also modified using a factor with a triangular distribution corresponding to ±10%, but the upper limit was set at 100 if 10% x CN > 100, since a CN greater than 100 would result in more runoff than rainfall.

Likewise, for tributary flows, daily flow values gaged at the sample collection site were multiplied by a triangular distribution with upper and lower value limits corresponding to ±10% of the daily value. Streams with daily flow extrapolated from gages at another location on the same stream were modified with a triangular distribution of ±20%. Streams were flow was estimated using the similar watersheds unit area approach were modified with a triangular uncertainty of ±30%.

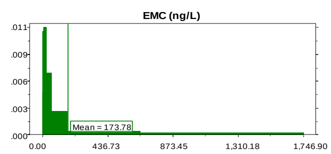
In the case of non-point sources, the authors of that report determined the percentiles of concentration in total PCBs. That information was included in the uncertainty analysis as a custom probability distribution. This distribution, shown in Figure 2.23, indicates a high likelihood of lower concentrations, but a high upper concentration limit.

Figure 2.23 - Custom Distribution of Total PCB Event Mean Concentration.

Assumption: EMC (ng/L) **Cell: E5**

Custom distribution with parameters:

				Relative Prob.
Continuous range	0.00	to	2.20	0.010101
Continuous range	2.20	to	5.85	0.040404
Continuous range	5.85	to	23.55	0.202020
Continuous range	23.55	to	61.99	0.252525
Continuous range	61.99	to	163.20	0.252525
Continuous range	163.20	to	656.93	0.202020
Continuous range	656.93	to	1,746.90	0.040404
Total Relative Probability				1.000000



To convert from total PCBs to penta-PCB, we multiplied the total PCB EMC by a conversion factor associated with the proportion of penta-PCB in overall domestic production (as discussed in Section 2.4.2). To express this conversion as an uncertainty, a second custom distribution was developed where the proportion of penta-PCB present (x axis) was represented by 5 discrete step functions corresponding to the 5 most common Aroclors. In this case, the relative probability (y axis) is determined by the % of domestic production of the Aroclor.

Figure 2.24 - Custom Distribution Representing the Proportion of penta-PCB and Relative Domestic Production for 5 Aroclors.

Custom distribution with parameters:		Relative Prob.
Aroclor 1016	0.01	0.131313
Aroclor 1242	0.06	0.525253
Aroclor 1260	0.09	0.111111
Aroclor 1248	0.20	0.070707
Aroclor 1254	0.56	0.161616
Total Relative Probability		1.000000

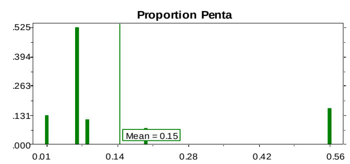
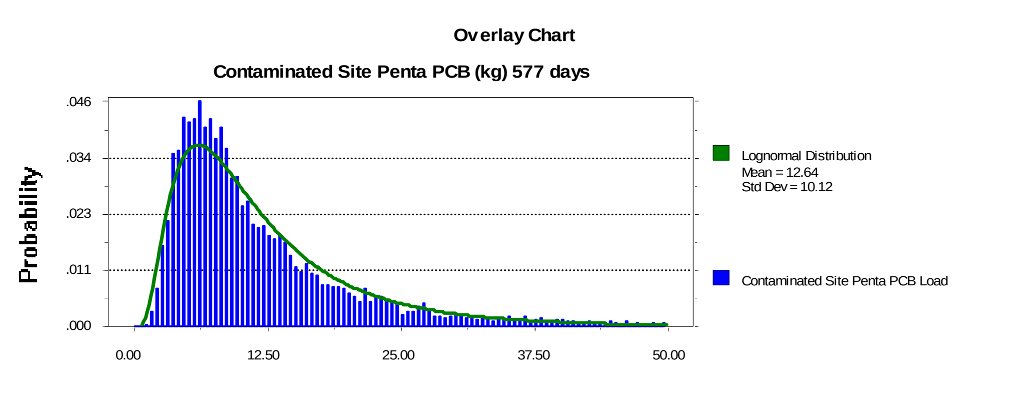
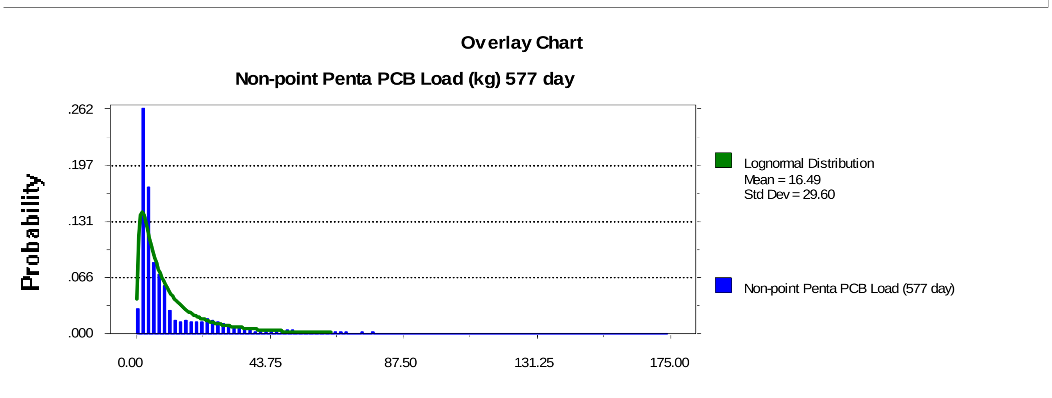
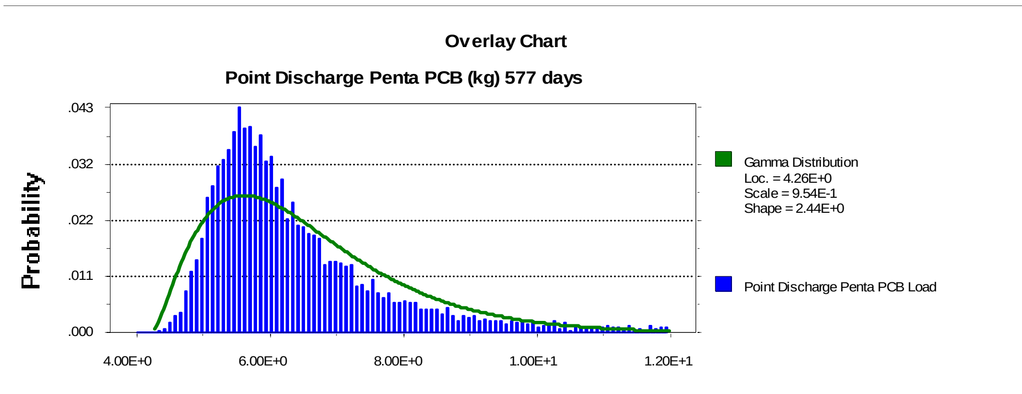


Figure 2.25 - Monte Carlo Analysis Results.







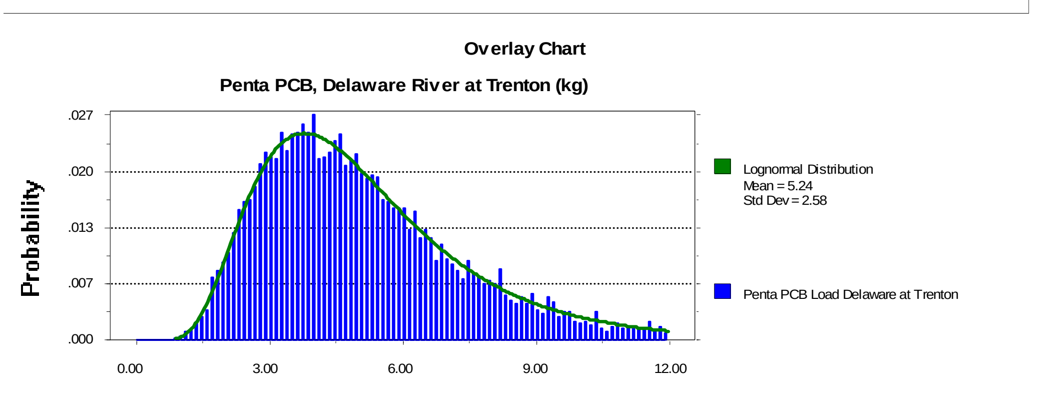
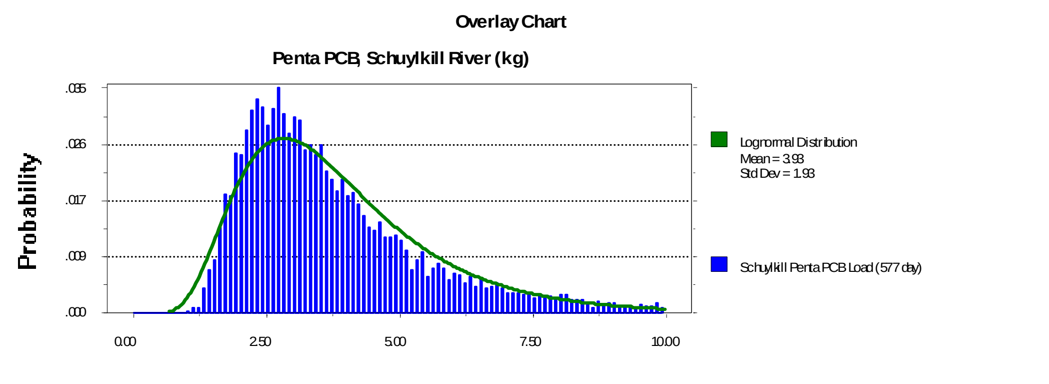
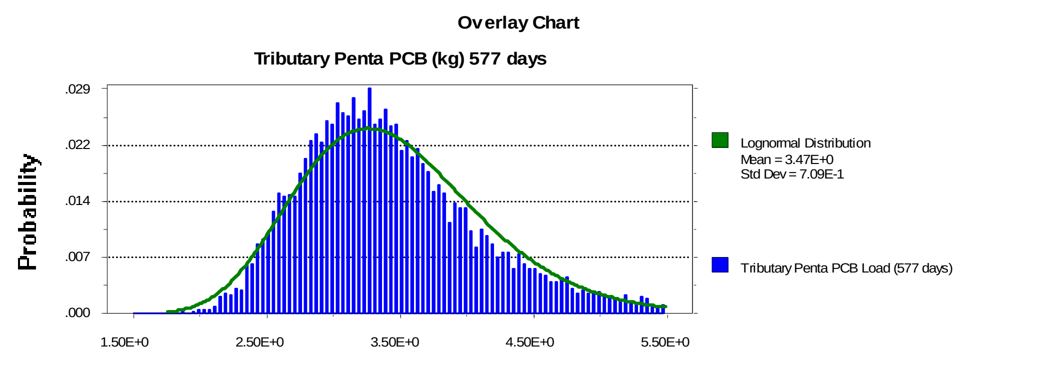
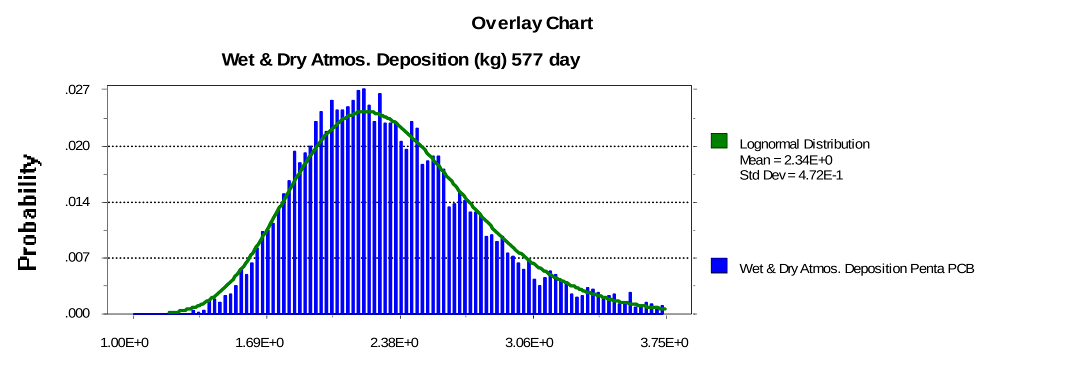
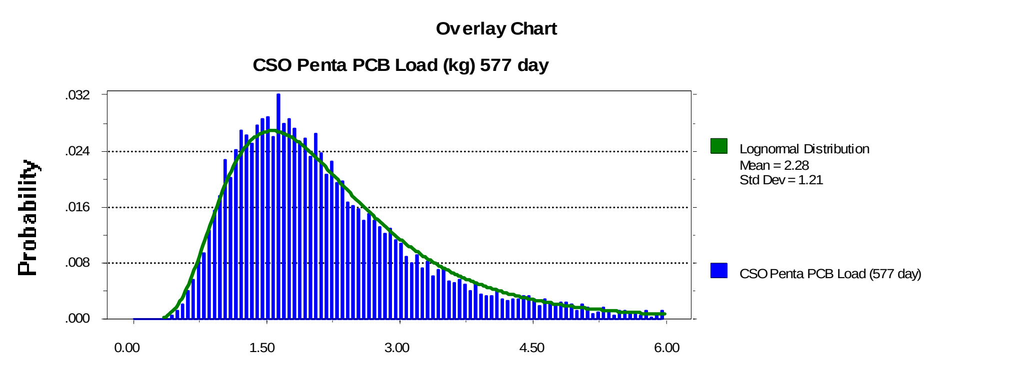


Figure 2.25 - Monte Carlo Analysis Results (Continued).









For each source category, 10,000 iterations of the 577-day penta-PCB load were computed. Results are shown in Figure 2.25. In Figure 2.25, the blue vertical bars show the results of the 10,000 iterations for each source category. The green curve depicts the probability distribution providing the closest match to the Monte Carlo analysis results. In some cases, the fitted distribution appears to match well (Delaware River at Trenton). In other cases, only an approximate match is possible (point discharges).

Figure 2.26 shows the uncertainty range, including the minimum and maximum computed 577-day penta-PCB load for each source category, as well as the 20th and 80th percentile loads. Table 2.16 shows the percentiles of the 577 day penta-PCB load for each source category. Note that since fluxes are most appropriately calculated within the model, they could not be included in this Monte Carlo analysis.

Figure 2.26 - Uncertainty Ranges surrounding 577 day penta-PCB Load Estimates by Source Category on a log scale

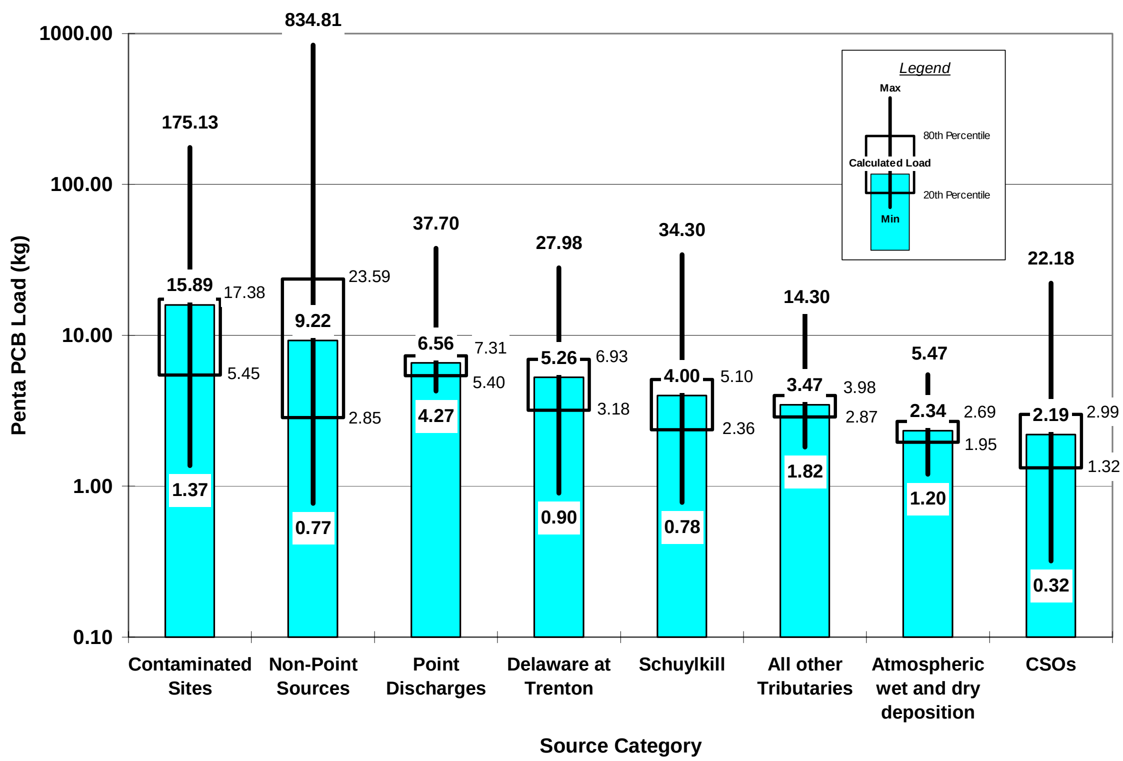


Table 2.16: Percentiles of penta-PCB Load for each Source Category as kilograms over 577 days

Percentile	Contaminated Sites	NPS	Point Discharge	Delaware at Trenton	Schuylkill	Other Tribs	Atmospheric Deposition	CSOs
0%	1.37	0.77	4.27	0.90	0.78	1.82	1.2	0.32
10%	4.23	2.28	5.16	2.59	2.01	2.66	1.8	1.08
20%	5.45	2.85	5.40	3.18	2.36	2.87	1.95	1.32
30%	6.60	3.56	5.61	3.68	2.68	3.04	2.06	1.54
40%	7.85	4.48	5.81	4.18	3.00	3.20	2.17	1.75
50%	9.19	5.94	6.04	4.70	3.35	3.35	2.27	1.97
60%	11.06	8.35	6.33	5.29	3.78	3.51	2.39	2.22
70%	13.62	12.26	6.73	5.99	4.32	3.71	2.53	2.54
80%	17.38	23.59	7.31	6.93	5.10	3.98	2.69	2.99
90%	24.94	44.82	8.53	8.52	6.61	4.42	2.95	3.82
100%	175.13	834.81	37.7	27.98	34.3	14.3	5.47	22.18

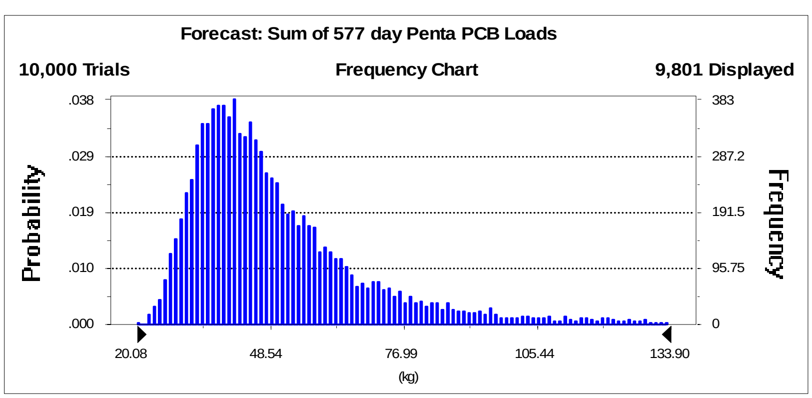
Once the 577-day penta-PCB load histograms are developed for each source category, the software used to perform the Monte Carlo analysis allows the user to find the probability distribution which most closely matches the histogram. By assigning a probability distribution to each source category 577-day load, we can estimate the overall loading uncertainty by again iteratively selecting and summing values from each source category distribution. Figure 2.27 shows the results of the Monte Carlo analysis of the sum of all source categories over 577 days. From these results it is apparent that while the uncertainties surrounding each source category are high, the central tendency for the overall loading is still grouped near the median value. While it is possible to draw a very high value for all source categories in a single iteration, the probability of this occurrence is low.

Figure 2.27 - Range and Distribution of 577-day sum of penta-PCB loads.

Forecast: Sum of 577 day Penta PCB Loads

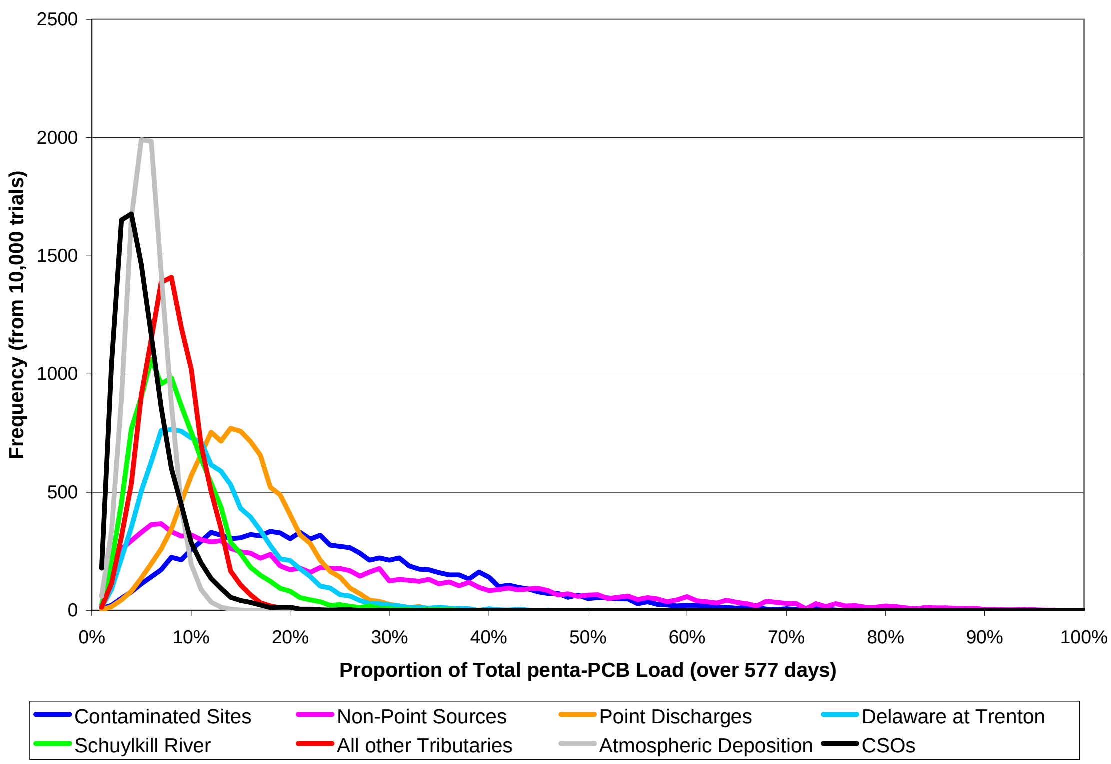
Summary:
Display Range is from 20.08 to 133.90 (kg)
Entire Range is from 20.08 to 701.80 (kg)
After 10,000 Trials, the Std. Error of the Mean is 0.30

Statistics:	Value
Trials	10000
Mean	52.85
Median	45.35
Mode	---
Standard Deviation	29.66
Variance	879.59
Skewness	5.44
Kurtosis	61.76
Coeff. of Variability	0.56
Range Minimum	20.08
Range Maximum	701.80
Range Width	681.71
Mean Std. Error	0.30



Iteratively drawing from the probability distribution of each source category also allows us to assess the probability distribution of the proportion of each source category to the overall load. Figure 2.28 shows the range and distribution of the proportion from each source category to the total. Likewise, Table 2.17 presents the percentiles of proportion for each source category. It should be noted that the proportion for each iteration was computed based on a total load for each iteration. That total computed load changed from iteration to iteration, depending on the relative loads drawn for each source category during that iteration. If a given source category represents a particularly high proportion for a single iteration, the other source categories would be proportionally low so that the sum of all the proportions for that iteration would equal 100%. Focusing on the 90th percentile, Table 2.17 shows that during 90% of the iterative computations, the contaminated site load was 42.7% or less of the total load, the non-point source load was 52.33% or less of the total load, the point discharge load was 21.44% or less of the total load, the Delaware at Trenton was 19.25% or less of the total load, and so on.

Figure 2.28 - Range and Distribution of the Proportion of Each Source Category to the 577-day total load of penta-PCBs



Finally, the uncertainty analysis provides some estimate of a reasonable upper and lower bound for loadings and forcing functions. To assess the model's sensitivity to load uncertainty, scaling factors equal to the total load divided by the 20^{th} percentile load (scaling factor = 0.78) and the total load divided by the 80^{th} percentile load (scaling factor = 1.39) were developed.

These scaling factors were then applied simultaneously to the following load categories:

- Contaminated Sites;
- Non-Point Sources;
- Point Discharges;
- Delaware at Trenton;
- Schuylkill;
- All other tributaries;
- Atmospheric wet and dry deposition; and
- CSOs.

This analysis applied only to loads. Other sources of penta-PCB, including the ocean boundary, the C&D canal, atmospheric gas concentration, and sediment concentration, were not scaled. The intent was to develop loads that were substantially higher and substantially lower than the current estimated loads, but still proportionally consistent with the current loading estimates and still within the realm of the expected upper and lower bound loadings. Using these scaled loads in the 577-day simulation period the model yielded the results shown in Figures 2.29 and 2.30. These figures show the water column concentrations of dissolved (as truly dissolved plus DOC-bound penta-PCB) and particulate penta-PCB relative to the unscaled concentrations for both the 20^{th} and 80^{th} percentile scaled load runs.

Table 2.17: Percentiles of the Proportion of Each Source Category to the 577-day total load of penta-PCBs

Percentile	Contaminated Sites	Non-Point Source	Point Discharge	Delaware at Trenton	Schuylkill	All Other Tributaries	Atmospheric Deposition	CSO
0%	0.64%	0.33%	0.59%	0.35%	0.22%	0.31%	0.22%	0.07%
10%	8.92%	4.39%	7.77%	4.74%	3.46%	4.10%	2.77%	1.91%
20%	12.55%	7.44%	9.85%	6.25%	4.61%	5.13%	3.48%	2.56%
30%	15.70%	10.61%	11.40%	7.53%	5.65%	5.96%	4.03%	3.14%
40%	18.79%	14.39%	12.78%	8.77%	6.58%	6.69%	4.53%	3.72%
50%	21.95%	18.52%	14.08%	10.09%	7.58%	7.41%	5.02%	4.33%
60%	25.65%	23.77%	15.41%	11.59%	8.65%	8.12%	5.52%	4.99%
70%	29.89%	30.17%	16.92%	13.37%	9.98%	8.96%	6.05%	5.83%
80%	35.00%	39.10%	18.73%	15.72%	11.76%	9.97%	6.70%	6.98%
90%	42.70%	52.33%	21.44%	19.25%	14.56%	11.45%	7.67%	8.88%
100%	84.40%	97.28%	39.00%	48.15%	35.28%	26.95%	15.71%	31.64%

It should be noted that the lines converge on the left hand side, in part, because the ocean boundary was not scaled. If the ocean boundary had been scaled, the lines would not converge. Since we consider the ocean boundary to be an inexhaustible source and sink, applying the 20th and 80th percentile scaling factors there would not be appropriate. In future phases of work, some other expression of uncertainty may be considered for the ocean boundary and C&D canal. Similarly, the sediment initial concentrations and gas phase air concentrations were not scaled. Figures 2.29 and 2.30 demonstrate that the effect of load uncertainty is most prominent at the upstream boundary at Trenton. The effect is somewhat mitigated in the remainder of the Zones, although some of that mitigation is attributable to the unscaled ocean boundary. Except for Zone 2, predicted water column concentrations with the scaled loads were within -10% to +20% of the unscaled loads. Since the sediment concentrations and air gas phase concentrations were not scaled, some additional model ramp up time was allowed, and the figures compare the median values for each of the 3 runs (baseline, 20th percentile scaled, 80th percentile scaled) for only the last 13 months of the full 19 month (577 day) simulation period.

Figure 2.29 - Model Dissolved PCB Sensitivity to Load Uncertainty

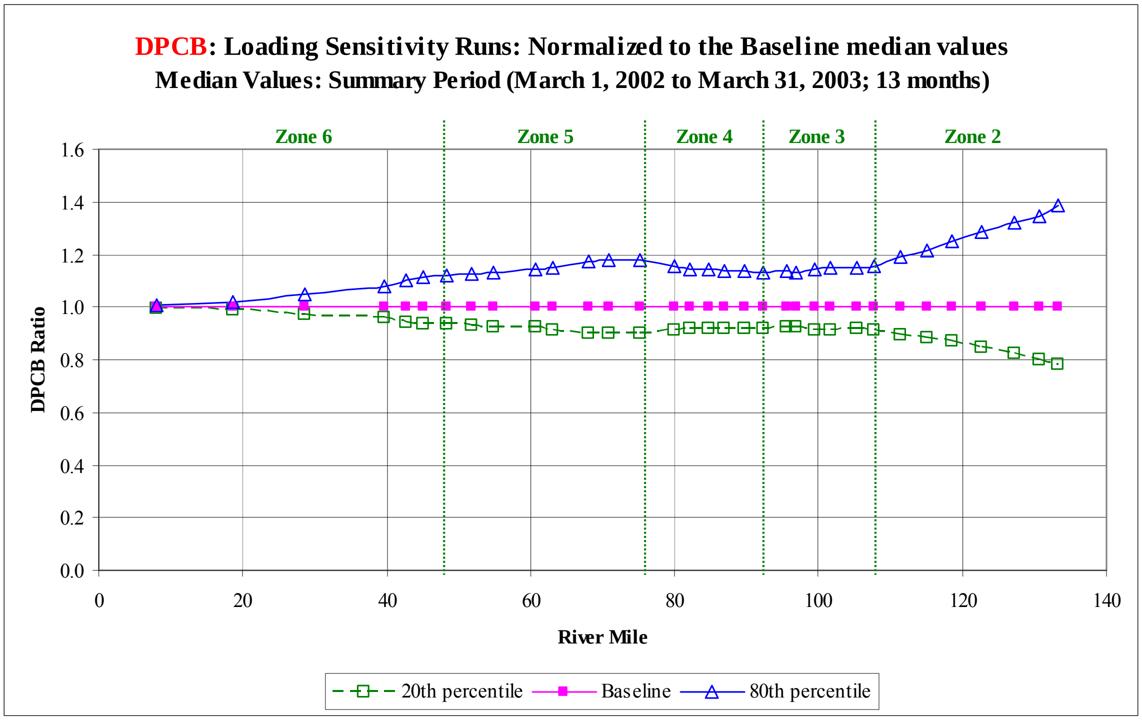
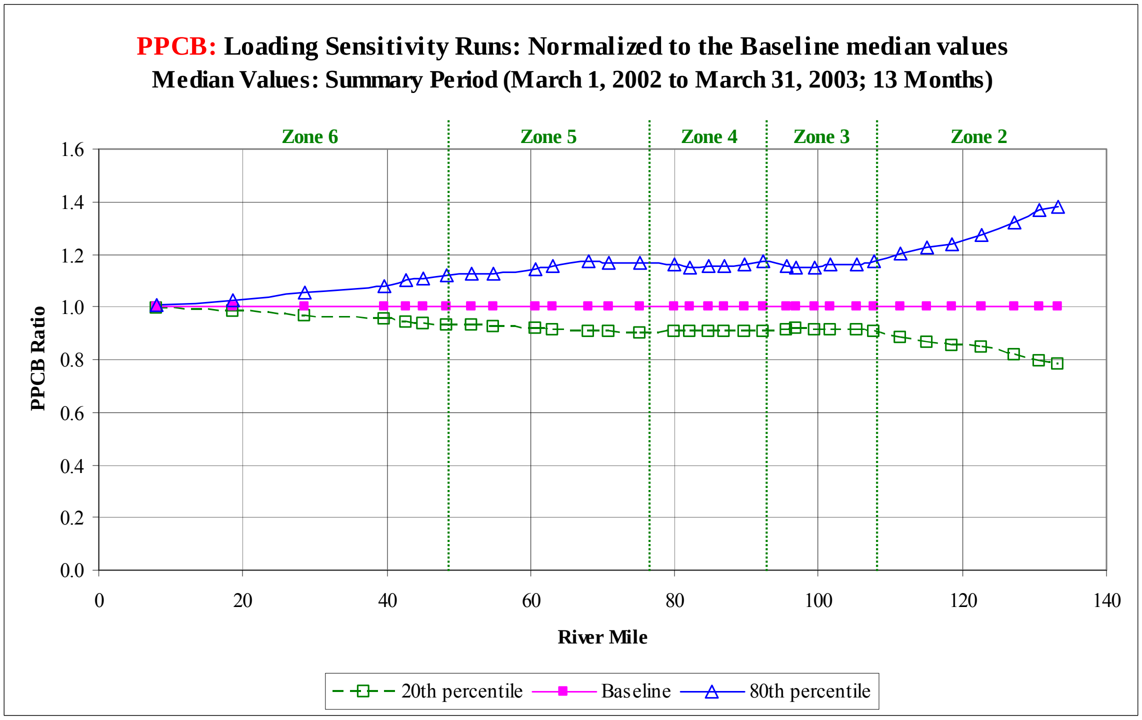


Figure 2.30 - Model Particulate PCB Sensitivity to Load Uncertainty



3 Ambient Water Quality and Sediment Data

3.1 Temporal and Spatial Design of Ambient Water Column Monitoring

To support development of the Delaware Estuary Polychlorinated Biphenyl Water Quality Model (DELPCB), accurate measurements of PCB concentrations and organic carbon in the Delaware Estuary were required. Ambient water samples were collected from the mainstem Delaware Estuary for the analysis of particulate and dissolved PCBs, total suspended solids, dissolved organic carbon (DOC), chlorophyll a, and particulate organic carbon (POC). The data collected allowed initial quantitation of dissolved and particulate PCB levels as well as organic carbon in the mainstem Delaware Estuary.

The objective of the monitoring was to measure PCB concentrations at low, high and intermediate flows in the portions of the Delaware Estuary listed for TMDL development. Initially the monitoring focused on Delaware Estuary Zones 2, 3, 4 and 5 but was expanded to include Zone 6 upon the recommendations of the PCB Model Expert Panel. One data set was obtained in September 18, 2001. The data from this date was used for water column initial condition in the model. Sampling started again on March 15, 2002 and continued until March 19, 2003. The data from these monitoring dates was used as calibration targets in the model. The sampling in Zone 2, 3, 4 and 5 was conducted within the limits of available funding. Fifteen main stem channel sites were sampled under high, low, and intermediate flows for a total of eight sampling events.

The additional monitoring in Zone 6 and lower Zone 5 was conducted concurrent with previously scheduled Delaware Estuary monitoring. The nine sample sites were sampled over five additional sampling events. The overall monitoring of ambient water column consisted of twenty-four sample stations in the estuary between river miles 6.5 and 131.1 during low, high and intermediate flow conditions. The sampling stations are listed in Table 3.1 and shown in Figure 3.1.

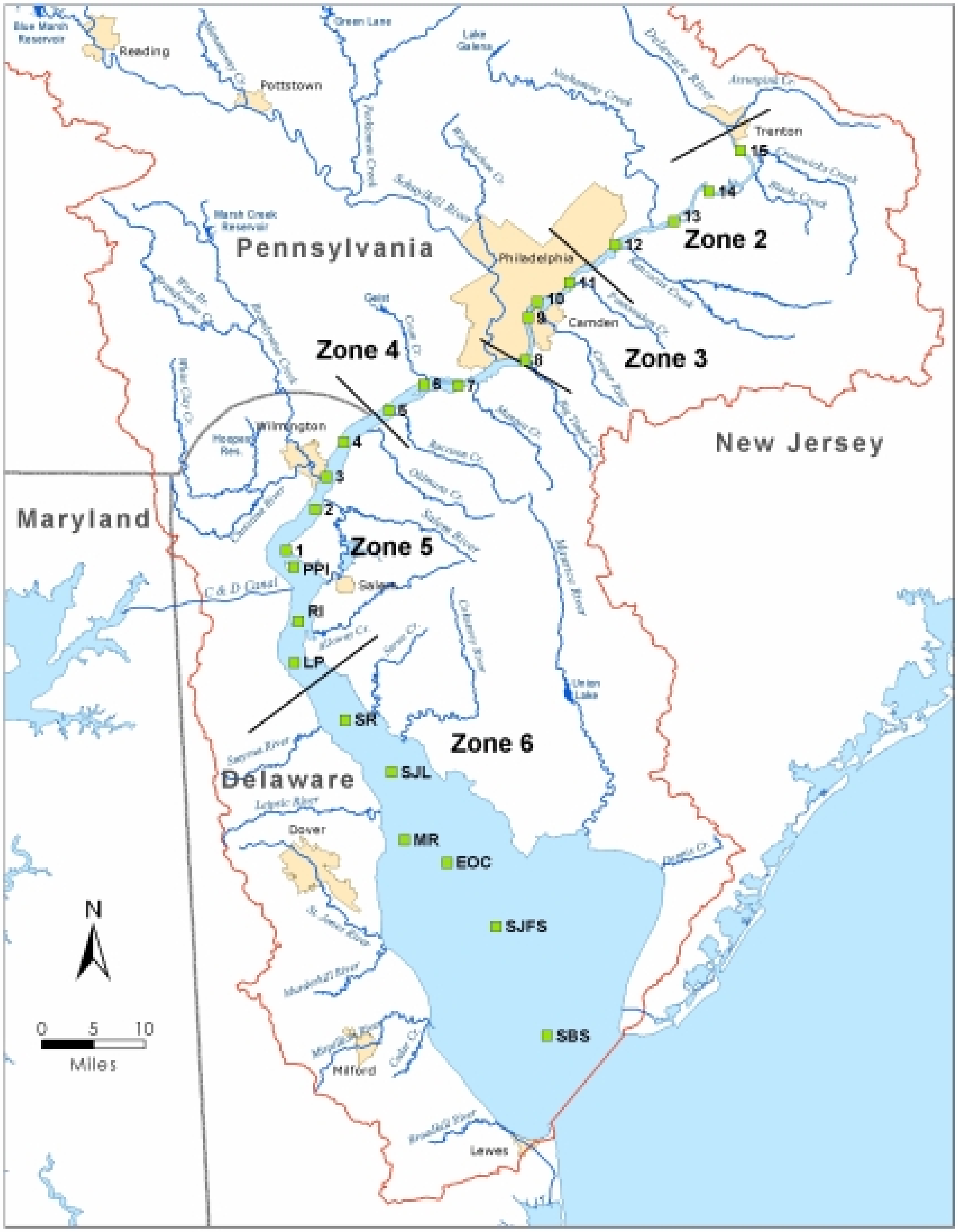
Table 3.1: Sampling Stations

SITE	RIVER MILE	SITE DESCRIPTION	DELAWARE ESTUARY ZONE	LATITUDE AND LONGITUDE
SBS	6.5	South Brown Shoal	Zone 6	38.54000 75.06049
SJFS	16.5	South Joe Flogger	Zone 6	39.04928 75.11311
EOC	22.75	Elbow of Cross Ledge	Zone 6	39.10802 75.16460
MR	31.0	Mahon River	Zone 6	39.11030 75.22020
SJL	36.6	Ship John Light	Zone 6	39.18100 75.23050
SR	44.0	Smyrna River	Zone 6	39.22650 75.28200
LP	48.2	Liston Point	Zone 6	39.27180 75.33360
RI	54.9	Reedy Island	Zone 5	39.30770 75.33350
PPI	60.6	Pea Patch Island	Zone 5	39.35580 75.33900
1	63.0	North of Pea Patch Isl	Zone 5	39.61430 75.57706
2	68.1	South of Del. Mem. Br.	Zone 5	39.67306 75.52414
3	70.8	North of Del. Mem. Br.	Zone 5	39.71908 75.50425
4	75.1	Opposite Oldmans Pt.	Zone 5	39.76868 75.47302
5	80.0	Opposite Mouth of Marcus Hook Cr.	Zone 4	39.81337 75.39057
6	84.0	Eddystone	Zone 4	39.85055 75.32709
7	87.9	Paulsboro	Zone 4	39.84871 75.26406

Table 3.1: Sampling Stations (*continued*)

SITE	RIVER MILE	SITE DESCRIPTION	DELAWARE ESTUARY ZONE	LATITUDE AND LONGITUDE
8	95.5	Opposite Mouth of Big Timber Creek	Zone 3	39.88522 75.14074
9	99.4	Penn's Landing	Zone 3	39.94547 75.13598
10	101.6	Opposite Cooper Point	Zone 3	39.96781 75.11932
11	105.4	Mouth of Pennsauken Cr.	Zone 3	39.99477 75.05978
12	111.5	Mouth of Rancocas Cr.	Zone 2	40.04830 74.97588
13	117.8	Burlington Bristol Br.	Zone 2	40.08142 74.86790
14	122.0	Florence	Zone 2	40.12398 74.80351
15	131.1	Biles Channel	Zone 2	40.18156 74.74505

Figure 3.1 - Ambient Monitoring Locations



3.1.2 Sampling Process Design

All samples were collected at a depth of 0.6 of the depth of the water column using a 10 liter Niskin water bottle. The water samples were collected by staff from the Delaware River Basin Commission (DRBC) and the Delaware Department of Natural Resources and Environmental Control. The locations sampled are listed in Table 3.1. One field blank and one trip blank was collected on each sampling day. At each location, samples were collected at three sites on a transect across the river, and composited into one sample per location. Samples were also collected from the site composites for solids, dissolved organic carbon, particulate organic carbon, chlorophyll-a, and turbidity. Air and water temperature, pH, salinity, conductivity, dissolved oxygen, and water transparency were also measured at each site on the transects at the time of sampling. Solids and organic carbon samples were shipped to the Chesapeake Biological Laboratory of the University of Maryland for analyses, while the turbidity and chlorophyll A samples were transported by the DNREC field crew to the DNREC laboratory for analysis. The composite sample from the river locations were shipped to Axys Analytical Services, Ltd. for PCB analysis.

3.1.3 Analytical Methods

Samples were analyzed for 124 PCB congeners, solids, POC, DOC, turbidity and chlorophyll-a as shown in Tables 3.2 below. Sample filtration, for dissolved constituents, was performed by the analytical laboratory.

Table 3.2: Summary of Analytical Parameters and Matrices

Analytical Parameter	Method	Matrix Analyzed
Particulate PCBs	Method 1668 Revision A : Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS	Solids retained on 1.0 µm nominal pore size glass fiber filter.
Dissolved PCBs	Method 1668 Revision A	Filtrate passed through 1.0 µm nominal pore size glass fiber filter.
Total Suspended Solids	Method No. 2540 D Standard Methods for the Analysis of Water and Wastewater, 19^{th} Ed.	Solids retained on 0.7 µm glass fiber filter.
Turbidity	Method 180.1, U.S. EPA, 1983	Whole water sample
POC	Method 440.0 Determination of Carbon and Nitrogen in Sediments and Particulates of Estuarine/Coastal Waters Using Elemental Analysis	Solids retained on 0.7 µm glass fiber filter.
DOC	Method No. 5310 C Standard Methods for the Analysis of Water and Wastewater, 19^{th} Ed.	Filtrate passed through 0.7 µm glass fiber filter.
Chlorophyll -a	Method 445 *In Vitro* Determination of Chlorophyll-a and pheophytin a in Marine and Freshwater Phytoplankton by Fluorescence	Solids retained on filter.

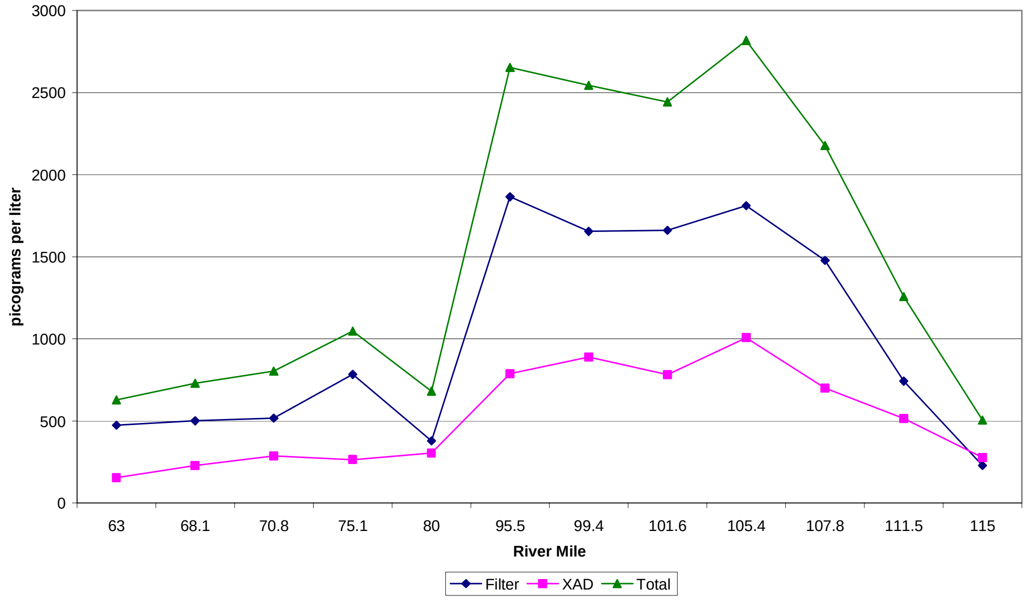
3.2 Monitoring Data

The information contained in this report is material received by the DRBC from analytical laboratories as of July 2003. Particulate organic carbon (POC) and PCB monitoring data are listed by sample date in Appendices 3A, 3B and 3C. Graphs of the particulate-PCB (filter), dissolved-PCB (XAD), and penta – PCB (total) data are also presented in Figures 3.2 through 3.8. The graphs are numbered from lowest to highest mean daily river flow at Trenton on the sampling dates. (See Section 3.3.1 for a descriptions of the penta-PCB components)

Figures 3.2 through 3.8 indicate that in general higher concentrations of penta-PCB are observed in low flow sampling dates. As the river flow increases the concentration of penta-PCB decreases. In the lower flow sampling events, the concentration of penta-PCB shows a pattern of elevated PCB between river miles 80 and 110 (Figures 3.2, 3.3, and 3.4) indicating PCB loadings in the urbanized areas of the river. A similar pattern of penta-PCB distribution is not observed in the higher flow sampling events (Figures 3.6, 3.7 and 3.8). In the higher flow sampling events, penta-PCB concentrations are lower and more evenly distributed over the sample area probably from dilution of PCB during high flow conditions.

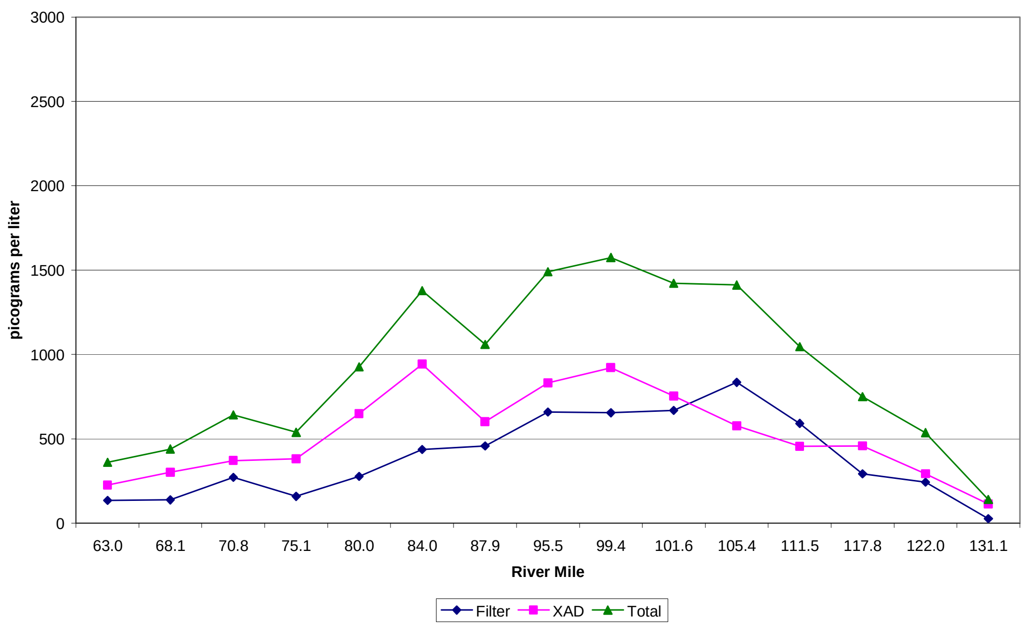
Also noteworthy is that dissolved and particulate penta-PCB are generally equivalent under intermediate flow conditions (Figure 3.7). The similar concentrations of dissolved penta-PCB (XAD) and particulate penta-PCB (filter) in the water column are not unexpected since total dissolved penta-PCB is defined as the sum of both truly dissolved and DOC bound penta-PCB. Therefore, higher concentrations in the total dissolved fraction are to be expected than would be the case in a truly dissolved fraction alone. However, dissolved and particulate PCB concentrations differ under the lowest and highest flow conditions measured. The particulate penta-PCB (filter) concentrations are higher under the lowest flow condition (Figure 3.2). The dissolved penta-PCB (XAD) concentrations are higher under the highest flow concentrations (Figure 3.8). The particulate penta-PCB (filter) fluctuate more with the river flow which is not unexpected.

Figure 3.2 – Ambient Water penta-PCBs, September 19, 2001



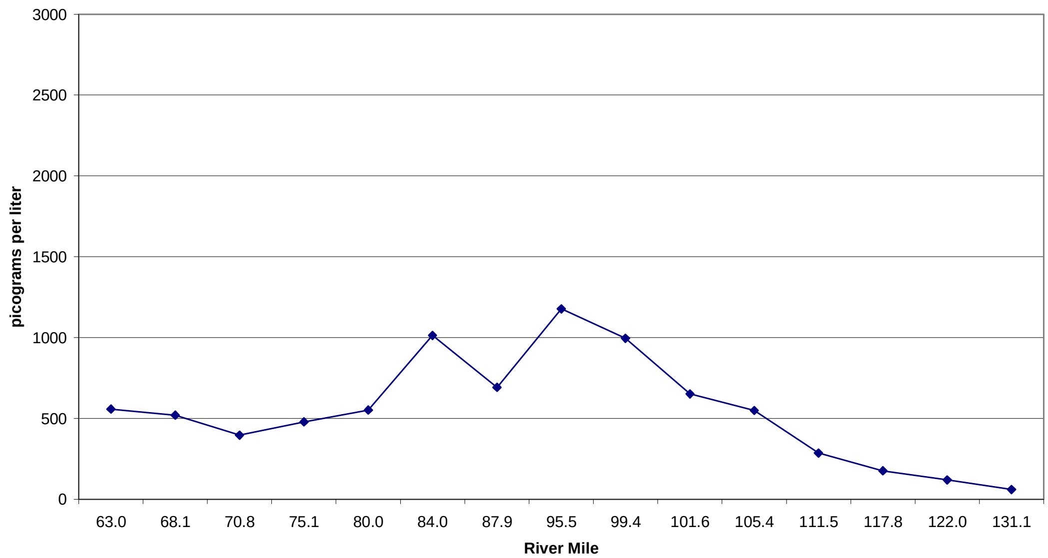
Mean Daily Flow 3,020 cfs

Figure 3.3 - Ambient Water penta-PCBs, October 8, 2002



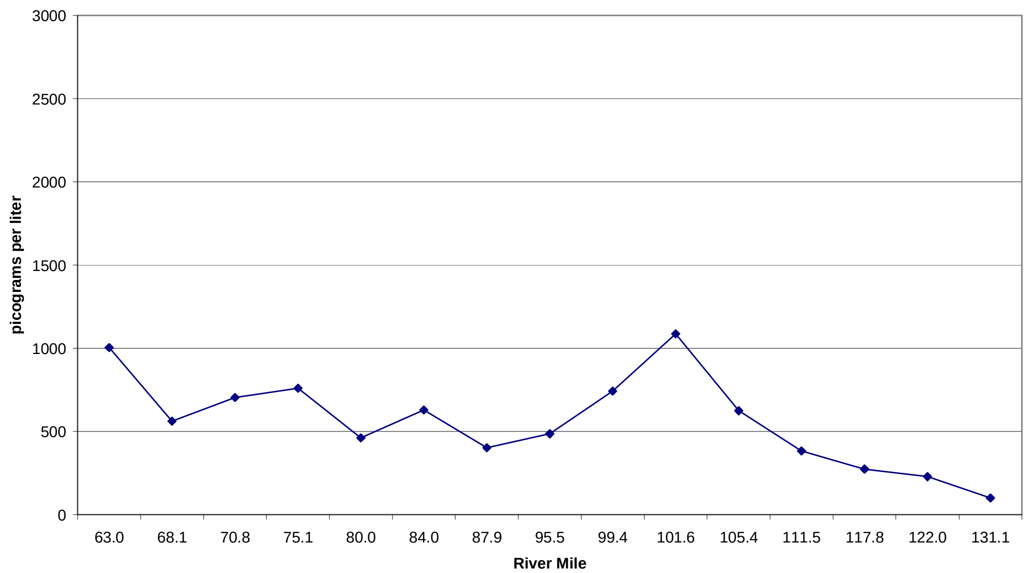
Mean Daily Flow 3,560 cfs

Figure 3.4 - Ambient Water penta-PCBs (filter only), April 11, 2002



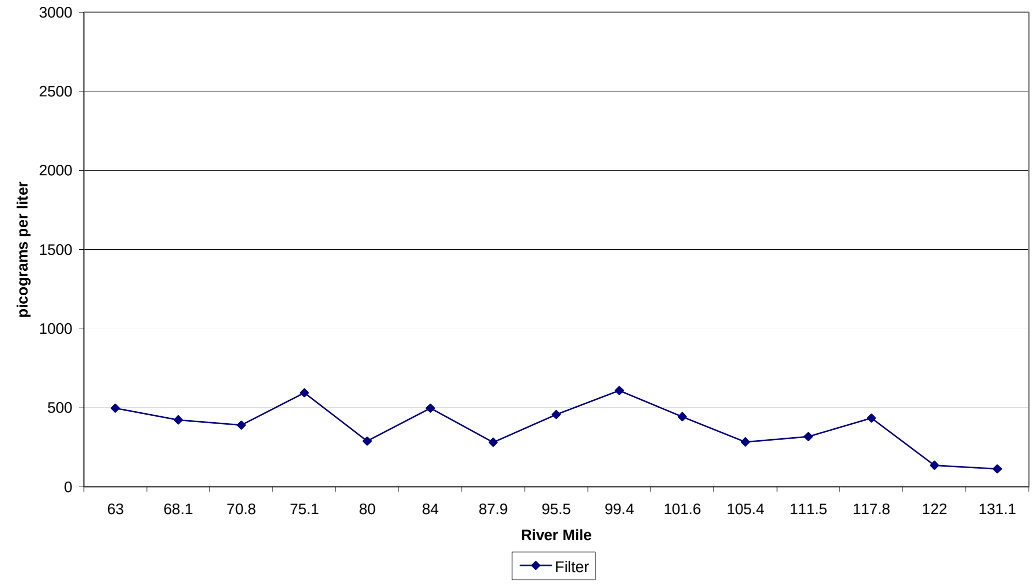
Ambient Water penta-PCBs (filter only), April 11, 2002 , Mean Daily Flow 7,980 cfs

Figure 3.5 - Ambient Water penta-PCBs (filter only), April 22, 2002



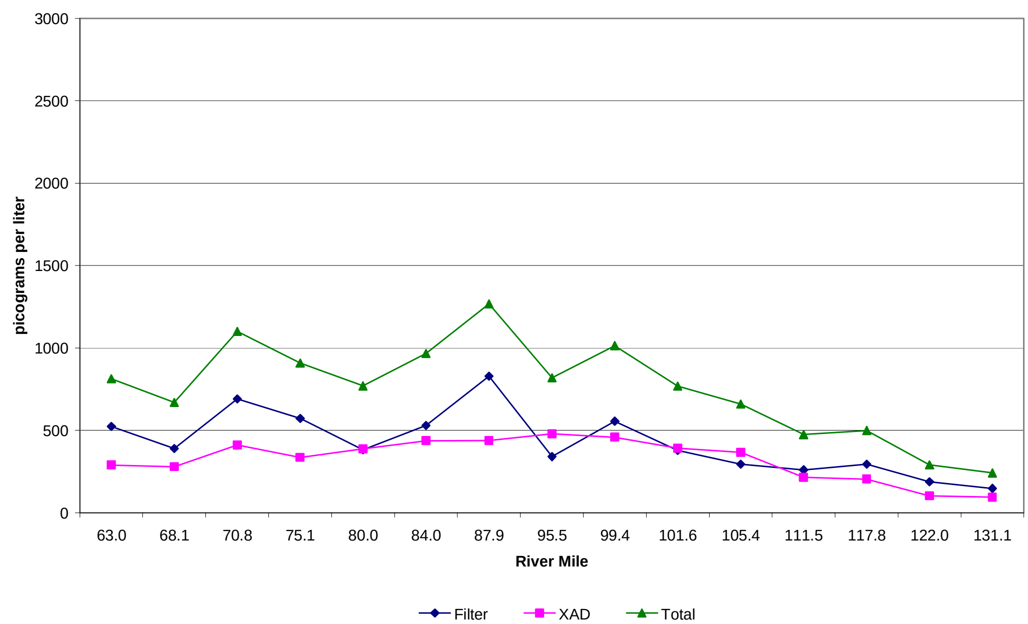
Daily Mean Flow 8,860 cfs

Figure 3.6 - Ambient Water penta-PCBs, June 19, 2002



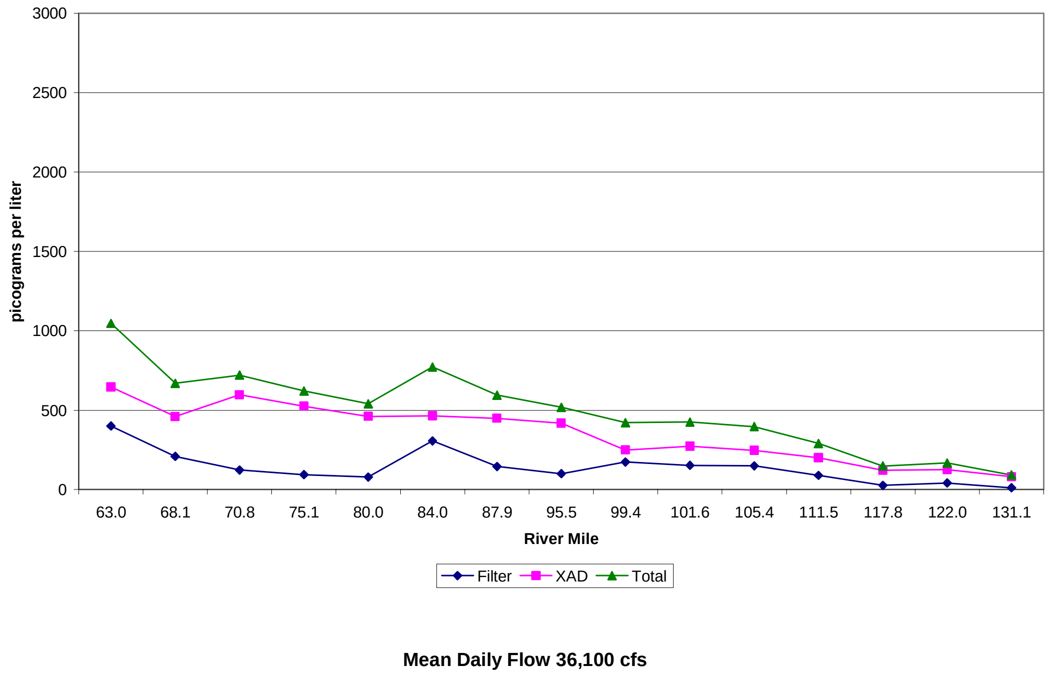
Daily Mean Flow 14,800 cfs

Figure 3.7 - Ambient Water penta-PCBs, May 6, 2002



Mean Daily Flow 16,100 cfs

Figure 3.8 - Ambient Water penta-PCBs, March 19, 2003



3.3 Development of Model Calibration Targets

The PCB Model Calibration Targets for Water Column (WC) and Surficial Sediment (S) Segment Ambient Water Quality is a compilation of observed and derived data used as calibration targets in the PCB model. The calibration targets are in three tables in Appendices A, B and C.

3.3.1 Water Column Calibration Targets

The water column data consists of total dissolved penta-PCB, particulate penta-PCB, the sum of all penta-PCB (total), and particulate organic carbon (POC) measured in ambient waters of the Delaware Estuary during the DRBC sampling period. All results for penta-PCB include the same 33 penta-congeners. A description of each component of PCBs in the water column data is as follows:

- The penta-PCB (total) in the water column is the sum of truly dissolved penta-PCB and DOC bound penta-PCB as well as particulate penta-PCB in the water column.

- The total dissolved penta-PCB is the sum of truly dissolved and DOC bound penta-PCB in the water column which is measured in the XAD fraction of Method 1668a.

- The WC-particulate penta-PCB is particulate bound penta-PCB in the water column which is measured in the > 1.0 µm filter fraction of Method 1668a.

Biotic carbon (BIC) in the calibration targets is derived from observed POC data based on a calculated estimate of the percent of POC that is BIC in the estuary. POC was measured concurrently with the PCB measurements. The estimate of the percent of POC that is BIC in the estuary was calculated at 12.25, 16.33, and 20.42% for carbon to chlorophyll-a ratios of 30, 40 and 50, respectively. These percentages were calculated based on the mean BIC/POC ratio for each carbon to chlorophyll-a ratio using observed chlorophyll-a data and observed POC data. Particulate Detrital Carbon (PDC) in the calibration targets is POC minus BIC. (See Section on Carbon to Chlorophyll Ratio)

3.3.2 Sediment Calibration Targets

The sediment data consists of penta-PCB, total organic carbon (TOC) and inorganic suspended solids (ISS) derived from several studies of sediment in the Delaware Estuary by the DRBC, NOAA, A.D. Little Inc. and Corp of U.S. Army Engineers. (See Section on Short Term Calibration Results) The sediment penta-PCB values are Zone medians of penta-PCB concentrations by dry weight sediment for each Zone converted to bulk volume (pg/L) to obtain the units used in the model. The TOC and ISS values are 13 bin rolling weighted averages of observed data.

For the 577 day short-term water quality model calibration, the sediment calibration "targets" are more accurately defined as sediment initial conditions. The details of the data averaging methods selected to define both the sediment penta-PCB and POC (essentially equivalent to TOC for the sediment bed) are presented in Section 3.4.2.

In order to normalize PCB for organic carbon in both the water column and sediment, R_1 and R_2 values were calculated for each segment of the model. R_1 is water column particulate-penta-PCB divided by the water column POC. R_2 is the sediment penta-PCB divided by sediment-TOC. These values are listed in Appendices A, B and C.

3.4 Initial Conditions

The WASP model framework requires that the user specify the starting concentration for each water column and sediment segment.

3.4.1 Water Column

Water column segments were set to the concentrations measured on 9/18/01 where the sample station was within the segment limits. We assumed a BIC/POC ratio of 16.33%, which corresponds to a *C/Chl* ratio of 40. The boundary segments for the Delaware at Trenton, Schuylkill, C&D Canal, and Ocean Boundary were set equal to the boundary concentrations on the first day of simulation (9/1/2001). Values for all other segments were linearly interpolated between the nearest upstream and downstream segments. Lateral segments other than the C&D canal and Schuylkill were set equal to the mainstem segment into which they discharge.

3.4.2 Sediment

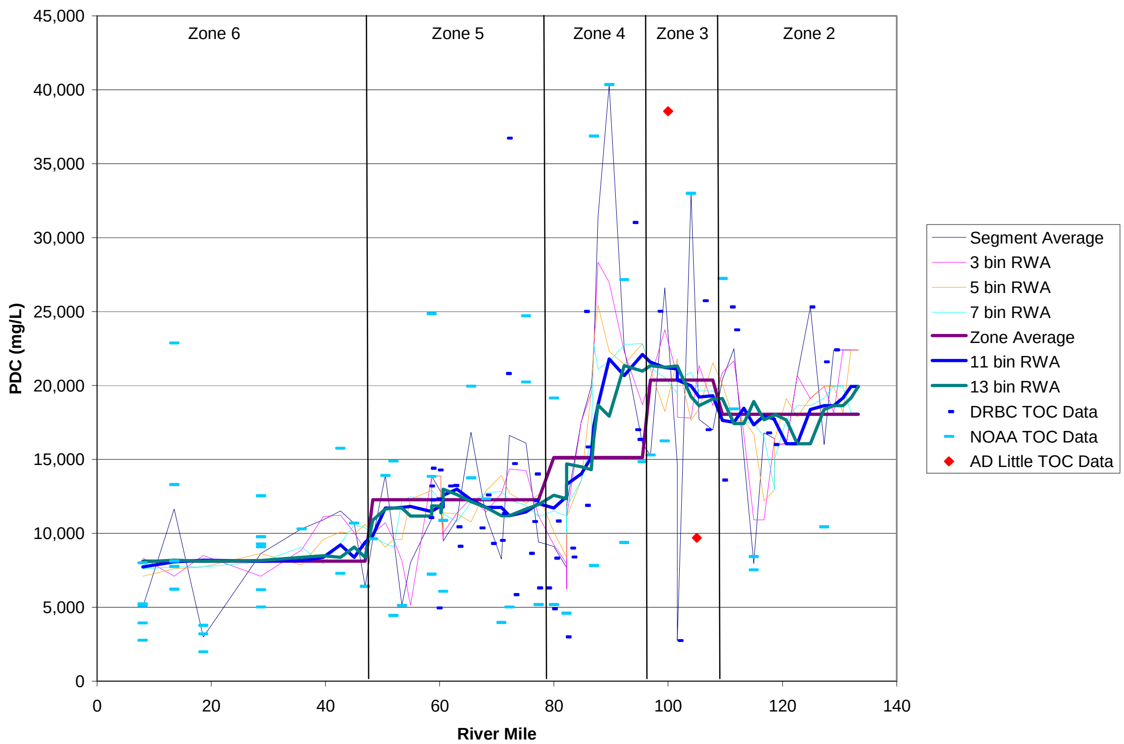
Sediment initial concentrations for the penta-PCBs, PDC, and inorganic solids (ISS) were estimated using existing surficial sediment data collected by DRBC, NOAA, the U.S. Army Corps of Engineers, and A.D. Little associates. Table 3.3 shows the available data for each model segment and zone.

Table 3.3: Inventory of Sediment Sample Results for Specifying Sediment Initial Conditions

Sediment Segment	Corresponding WC Segment	River Mile	Zone	No. of Sediment Samples DRBC	NOAA	COE	AD Little	Total
163	76	133.3	2					
162	75	132	2					
161	74	130.6	2					
159	72	129	2	1				**1**
158	71	127.3	2	1	1			**2**
157	70	124.9	2	1				**1**
156	69	122.6	2					
155	68	120.7	2	1				**1**
153	66	118.6	2	1				**1**
154	67	118.6	2					
151	64	116.8	2	1				**1**
150	63	115	2		2			**2**
149	62	113.2	2					
147	60	111.5	2	2	1			**3**
146	59	109.5	2	1	1			**2**
145	58	107.8	3	1				**1**
143	56	105.4	3	1			1	**2**
142	55	104	3		1			**1**
139	52	101.6	3	1				**1**
140	53	101.6	3					
138	51	99.4	3	1	1		1	**3**
136	49	96.9	3		1			**1**
135	48	95.5	4	2	1			**3**
131	44	92.3	4	1	2			**3**
130	43	89.7	4		1			**1**
128	41	87.7	4					
129	42	87	4		2	1		**3**
126	39	86.5	4					
125	38	84.8	4	3				**3**
122	35	82.2	4					
123	36	82.2	4	3	1			**4**
124	37	82.2	4					
121	34	80	4	4	2	1		**7**
120	33	77.3	5	3	1			**4**
119	32	75.1	5	2	2			**4**
118	31	72.2	5	4	1			**5**
112	25	70.8	5	2	1			**3**
111	24	68.1	5	3	1			**4**
110	23	65.5	5		2			**2**
109	22	63	5	3				**3**
107	20	60.6	5	3	2			**5**
108	21	60.6	5					
105	18	60.2	5					
106	19	60.2	5					
100	13	58.6	5	5	3			**8**
101	14	58.6	5					
99	12	54.9	5					
165	78	53.4	5		1			**1**
98	11	51.9	5		2			**2**
164	77	50.5	5		1			**1**
89	2	48.3	5		1	1		**2**
167	80	46.9	6		1			**1**
104	17	45	6		1			**1**
174	87	42.6	6		2			**2**
168	81	39.6	6					
169	82	35.8	6		1			**1**
170	83	28.7	6		6			**6**
171	84	18.6	6		3			**3**
173	86	13.5	6		5			**5**
172	85	8	6		5			**5**

In order to estimate sediment values in segments without sample results, and to address sediment heterogeneity, several approaches for interpolating and grouping sediment data were tested. These approaches included zone median values, zone mean values, and rolling weighted means using several different bin sizes. Ultimately, we determined that a 13 bin rolling weighted mean for PDC and ISS yielded the most reasonable sediment results for these values, and a zone median yielded the most reasonable results for penta-PCB. Furthermore, zone median penta-PCB specification is consistent with establishment of a zone by zone TMDL anticipated for this project. A 13 bin rolling weighted average PDC concentration allows for specification of each segment while maintaining and more accurately portraying the gradual shift in sediment composition from the head of tide to the mouth of the bay evidenced by the data. Figure 3.9 shows a comparison of several different methods for specifying sediment PDC concentrations.

Figure 3.9 - Comparison of Methods for Specifying Sediment Initial PDC Values



Since different data sets were analyzed for different numbers of penta-PCB congeners, it was necessary to identify an appropriate scaling factor to adjust all the data sets to the same basis. For example, the NOAA data set included analysis of 4 penta-PCB congeners, while the DRBC data set included analysis of 20 congeners. To estimate this scaling factor, we sub-sampled the DRBC results using only the congeners analyzed in the other data sets, and compared these results to the results using the sum of the DRBC congeners. A strong linear relationship suggests that the other data sets could be scaled up by multiplying the penta-PCB results by the slope of a line fit through those data points. Figure 3.10 shows this analysis conducted for the NOAA data set. Thus by multiplying the NOAA penta-PCB results by a factor of 2.8376, we can approximate what those results would have been if 20 congeners had been analyzed. Similar comparisons were conducted for both the Corps of Engineers and A.D. Little data sets as well.

Figure 3.10 - Comparison of the penta-PCB as the sum of DRBC congeners and the Sum of NOAA Congeners using the DRBC data Set

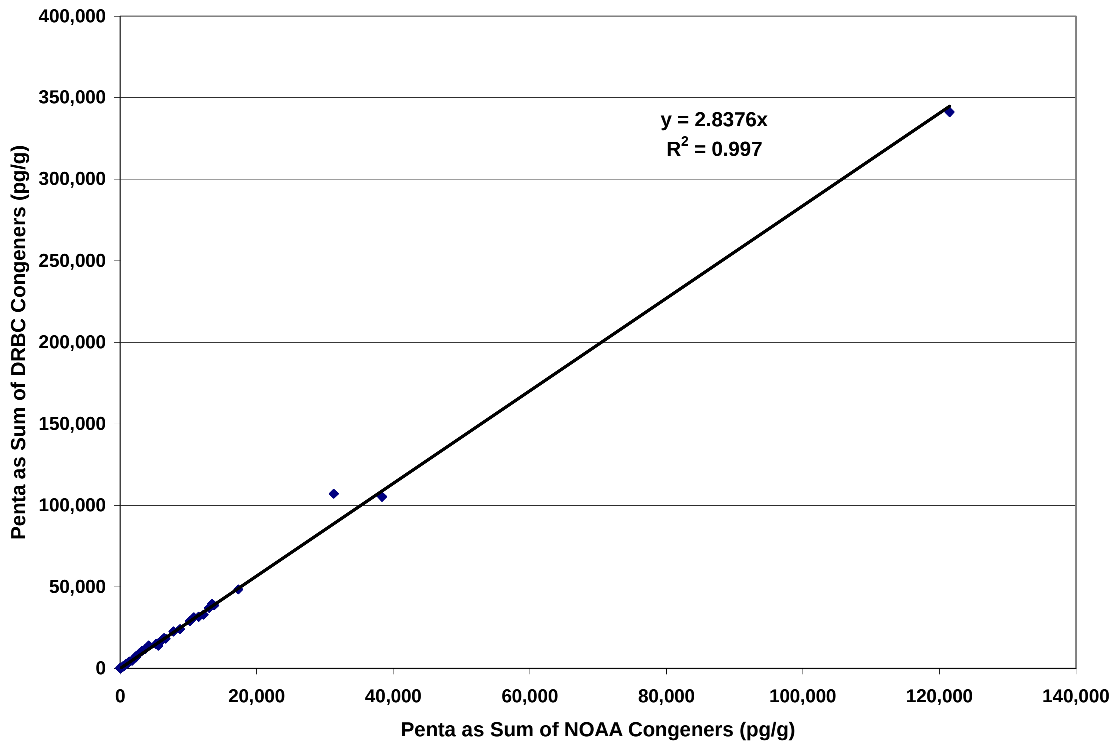
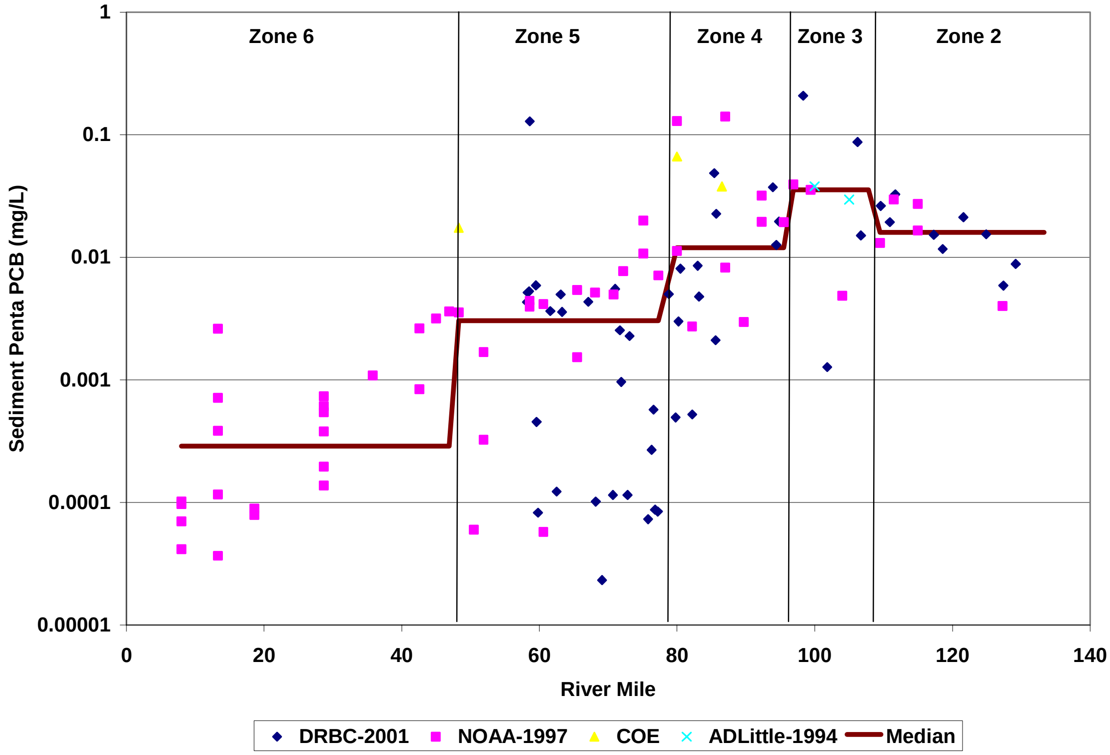


Figure 3.11 shows the sediment penta-PCB concentrations from the 4 data sets used and computed zone median penta-PCB values. Note that the general agreement between the DRBC data set and NOAA data set in range and distribution tends to support the scaling method described above.

Figure 3.11 - Sediment penta-PCB Data and Computed Zone Median Values



4 Short Term Calibration Results

As discussed in the report entitled "PCB Water Quality Model for the Delaware Estuary," DRBC and LTI have enhanced EPA's Water Quality Simulation Program (WASP) Version 5.12 to develop a general purpose sorbent dynamic PCB model for the Delaware River Estuary. The model simulates tidal flows, and spatial and temporal distributions of OC and PCB. This model incorporates one dimensional hydrodynamic flow with biotic carbon (BIC) and particulate detrital carbon (PDC) state variables as well as one inorganic solid as a pseudo-state variable. In this model, PCBs partition to particulate-PCB (by sorbing to BIC and PDC), truly dissolved-PCB, and dissolved organic carbon (DOC) bound-PCB phases. The inorganic solid pseudo-state variable is not a sorbent; it serves only to ensure that sediment bulk density, porosity, and burial rate are accurately calculated at each time step. As with the standard EPA WASP5-TOXI model, this model is capable of simulating up to three PCB state variables. In this study, we examined and evaluated the transport and fate of penta-PCB, for the reasons presented in Section 1. In the figures shown below, the PCB phases are abbreviated as follows:

particulate PCB	=	PPCB
total PCB	=	TPCB
truly dissolved PCB	=	DPCB
DOC-bound PCB	=	DOCPCB
Sum of truly dissolved PCB and DOC-bound PCB	=	DDPCB

The model treats the two OC sorbents as non-conservative state variables that are advected and dispersed among water segments, settle to and erode from benthic segments, move between benthic segments through net sedimentation or erosion, and decay at specified rates. BIC decays to PDC and PDC decays to DOC. However, since the concentration of DOC in both water column and benthic segments is fixed, the DOC concentration is not changed by PDC decay. Mass balance computations are performed in benthic compartments as well as water column compartments.

Following the calibration procedures indicated in Section 1, the input parameter values shown in Table 4.1 were selected. These parameters, when combined with the loadings and forcing functions (discussed in Section 2 of this report) within the model framework yield a model that predicts values closely matching the water column observations made during the calibration period. It should be noted that no calibration of penta-PCB partitioning coefficients or decay rates or adjustment of penta-PCB forcing functions was required to obtain a good fit between simulated and observed concentrations. This section includes selected comparisons of model results to observed and derived organic carbon (i.e. BIC and PDC) and PCB concentrations in the water column to illustrate model goodness-of-fit. A complete collection of comparisons are included in Appendices D and E.

Table 4.1: Input Parameters and Values for the PCB Water Quality Model

Parameter	Description	Value	Unit	Source
Vsbic	BIC Settling Velocity	0.1	m/day	Calibration
Vspdc	PDC Settling Velocity	1.0	m/day	Calibration
Vrpdc	PDC Resuspension Velocity	0.10-1.50	cm/yr	Calibration
m2	Sediment Solids	70,000-120,000	mg/L	Site specific data
PDCs	PDC Concentration -Sediment	8,000-22,000	mg/L	Site specific data
Kdbicw	BIC Decay rate	0.2	1/day	Calibration
Kdpdcw	PDC Decay rate-Water	0.05	1/day	Calibration
Kdpdcs	PDC Decay rate- Sediment	0.00026	1/day	Estimated from site specific SOD measurements
DOCw	Dissolved organic carbon-water column	4 - 9	mg/L	Site specific data
DOCs	Dissolved organic carbon-Sediment	10	mg/L	Literature
Koc	Partition Coefficient- organic carbon	6.26	logL/kg	Literature
Kdoc	Partition Coefficient-DOC	5.26	logL/kg	Estimated as 10% K_{OC}
El	Longitudinal dispersion coefficient	0 -250	m^2/sec	Calibration
Ev	Vertical diffusivity between sediment and water column	1.00E-08	m^2/sec	Literature
	Vertical diffusivity between surface and deep sediments	1.00E-10	m^2/sec	Assumed to be molecular diffusion rate

Figure 4.1 - Longitudinal Comparison of Simulated and Derived BIC Concentration

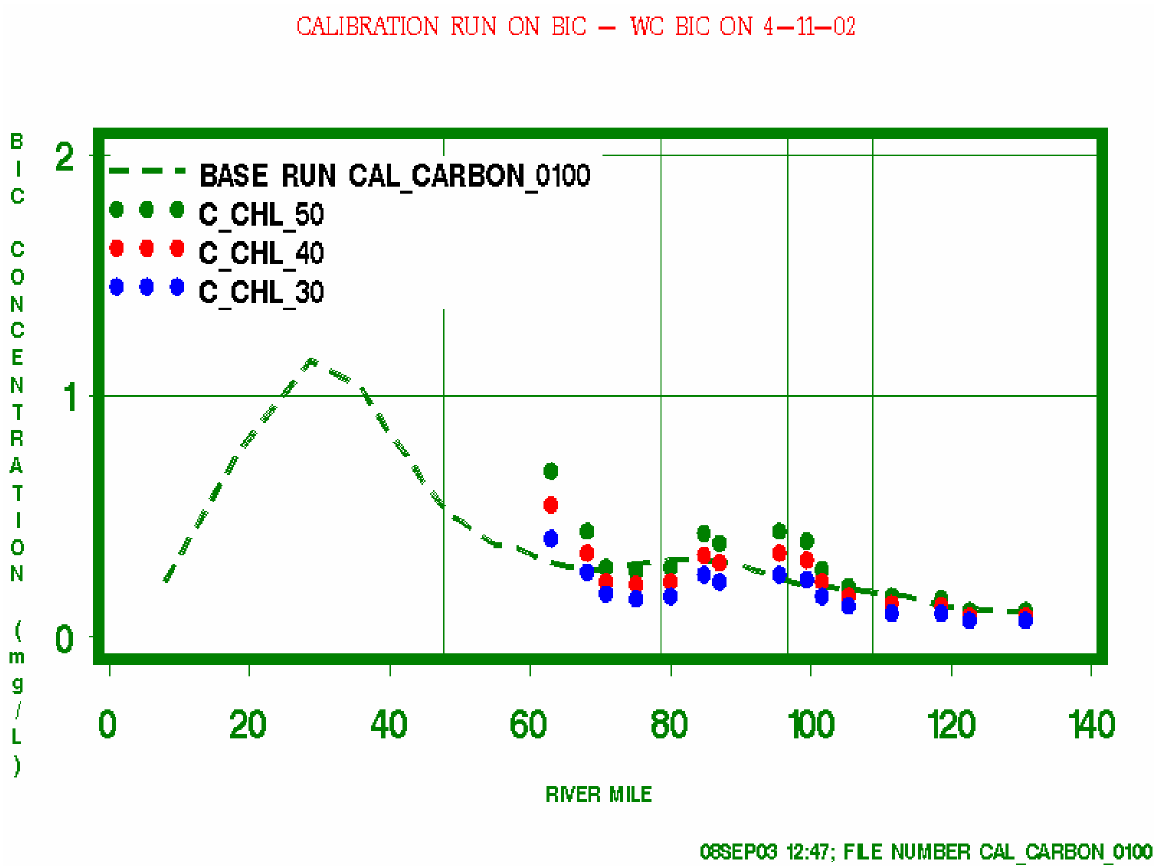


Figure 4.1 shows a comparison of simulated BIC and BIC derived from POC measurements and the data-estimated range for the carbon to chlorophyll ratio (30 to 50). Vertical lines indicate the water quality management zones, with:

Zone 2	From River Mile (RM) 133.4 to 108.4
Zone 3	From RM 108.4 to 95.0
Zone 4	From RM 95.0 to 78.8
Zone 5	From RM 78.8 to 48.2
Zone 6	From RM 48.2 to 6

Note there is a slight deviation in Zone 5. This deviation is apparent in several of the OC model to data comparisons. Likely causes include unaccounted for carbon load in the vicinity of Zone 5 (possibly from the C&D canal), or the effects of two layer estuarine circulation not fully described with a one dimensional hydrodynamic model.

Figure 4.2 - Longitudinal Comparison of Simulated and Derived PDC Concentration

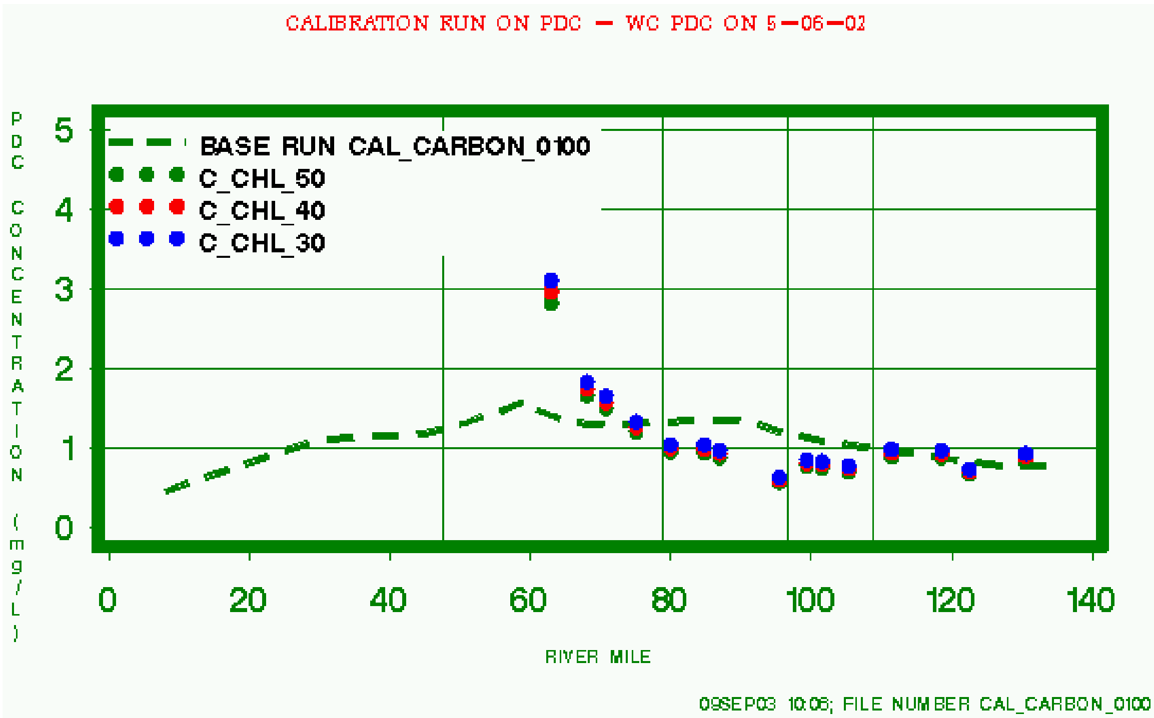


Figure 4.2 shows a comparison of simulated PDC and observed PDC (derived from POC measurements). Note again a deviation in Zone 5 and some deviation near the Zone 3 – Zone 4 divide.

Figure 4.3 - Longitudinal Comparison of Simulated and Derived PDC Concentration at Downbay Sites

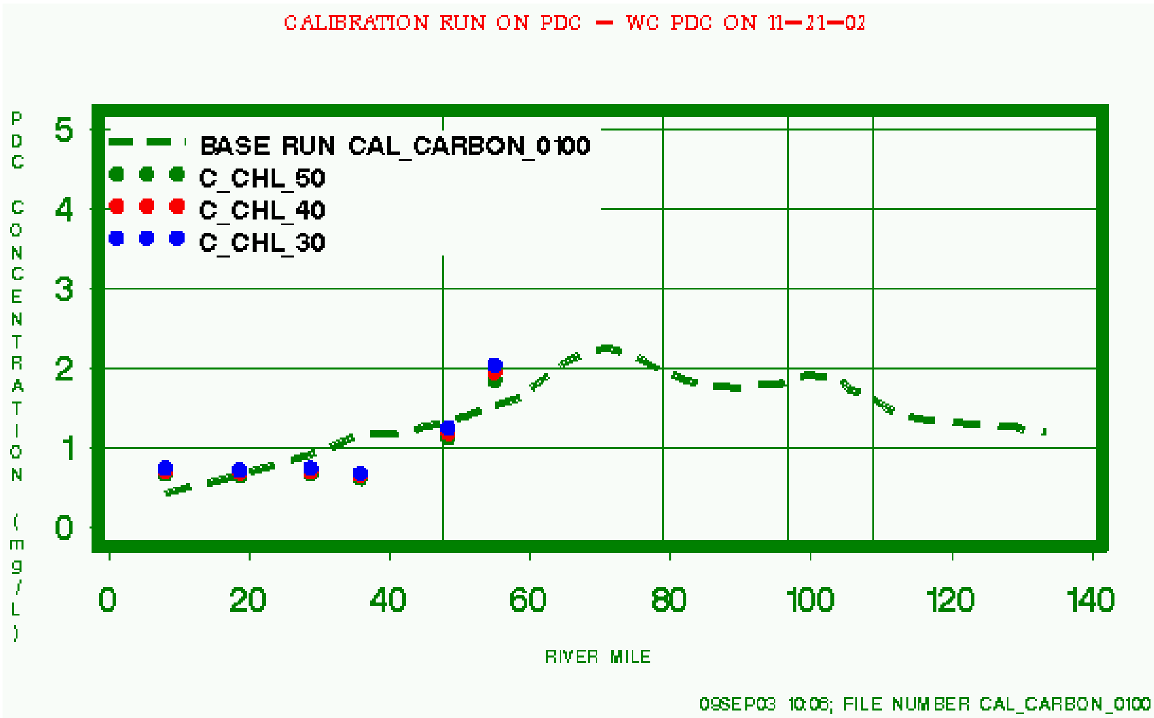


Figure 4.3 shows a comparison of simulated PDC and observed PDC (derived from POC measurements) in the downbay portion of the estuary.

Figure 4.4 - Longitudinal Comparison of Simulated and Observed Total (Particulate + Dissolved) penta-PCB Concentrations

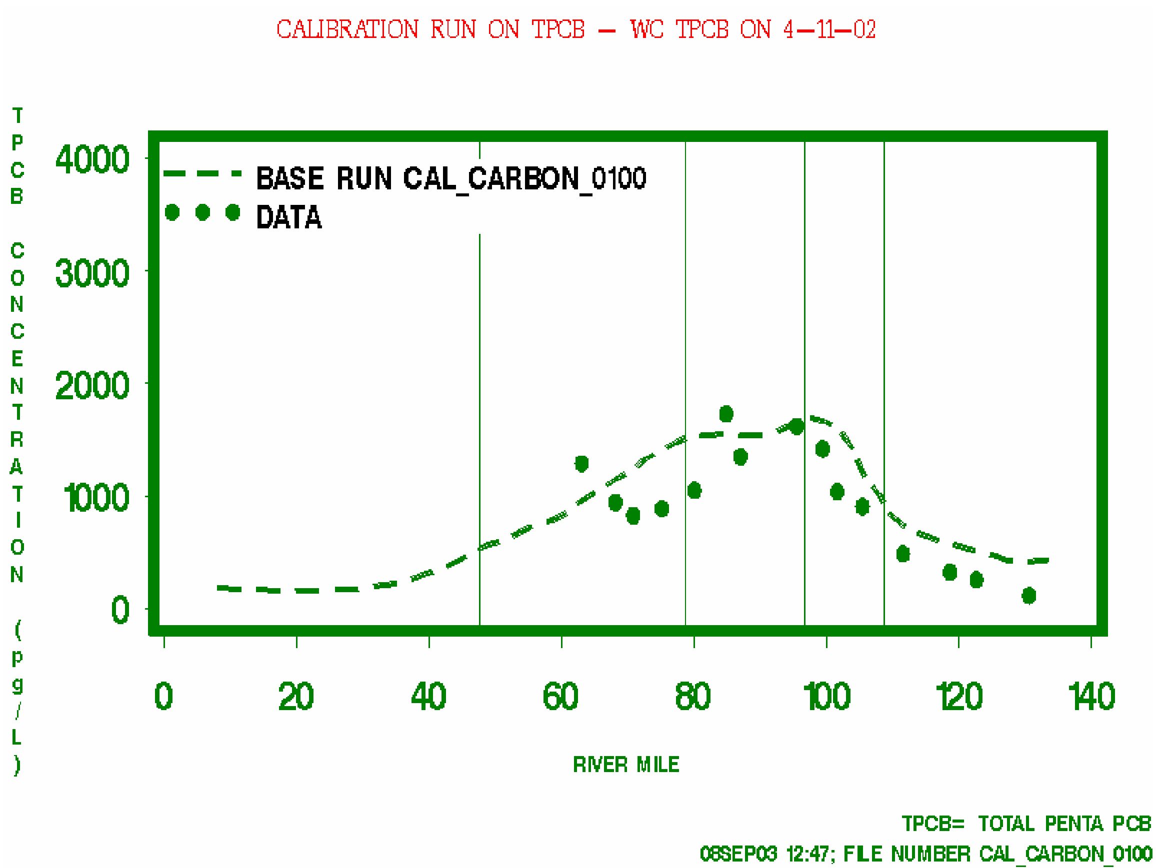


Figure 4.4 shows a comparison of simulated and observed total penta-PCB (particulate plus dissolved) water column concentrations.

Figure 4.5 - Longitudinal Comparison of Simulated and Observed Total (Particulate + Dissolved) penta-PCB Concentrations at Downbay Sites

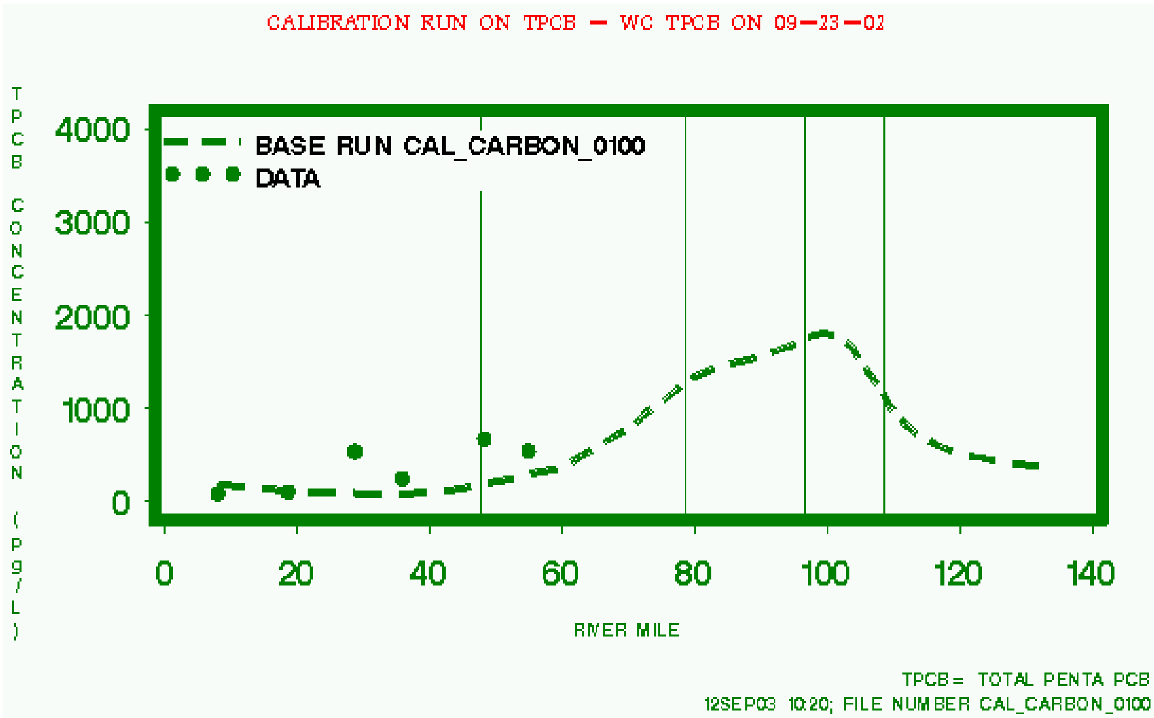


Figure 4.5 shows a comparison of simulated and observed total penta-PCB (particulate plus dissolved) water column concentrations at the downbay monitoring locations.

Figure 4.6 - Longitudinal Comparison of Simulated and Observed Particulate penta-PCB Concentration

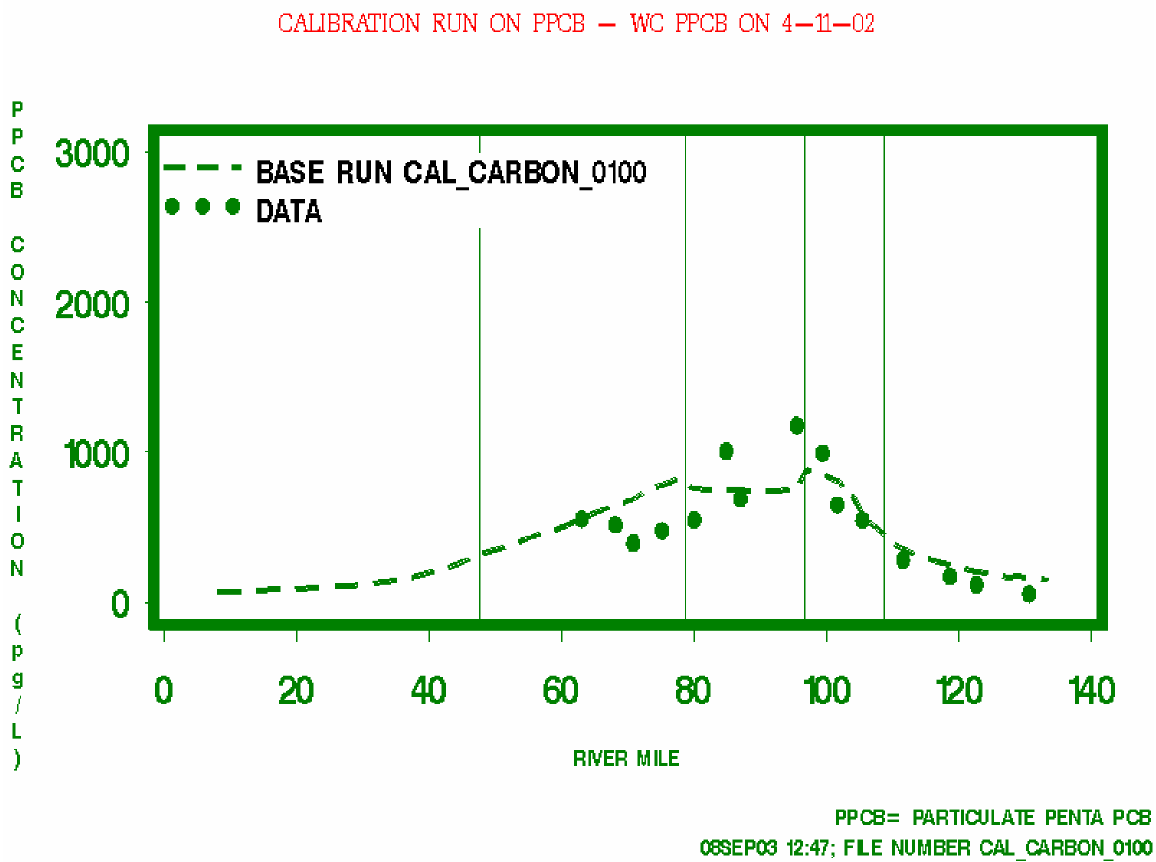


Figure 4.6 shows a comparison between simulated and observed particulate penta-PCB water column concentrations. While Zones 2 and 3 appear to match well, some underprediction is apparent in Zone 4 and some overprediction is apparent in Zone 5. This may be associated with unaccounted for PCB loads, or with the carbon deviations seen in the previous figures. The longitudinal trends of particulate penta-PCB reflect the trends of BIC and PDC.

Figure 4.7 - Longitudinal Comparison of Simulated and Observed Particulate penta-PCB Concentration

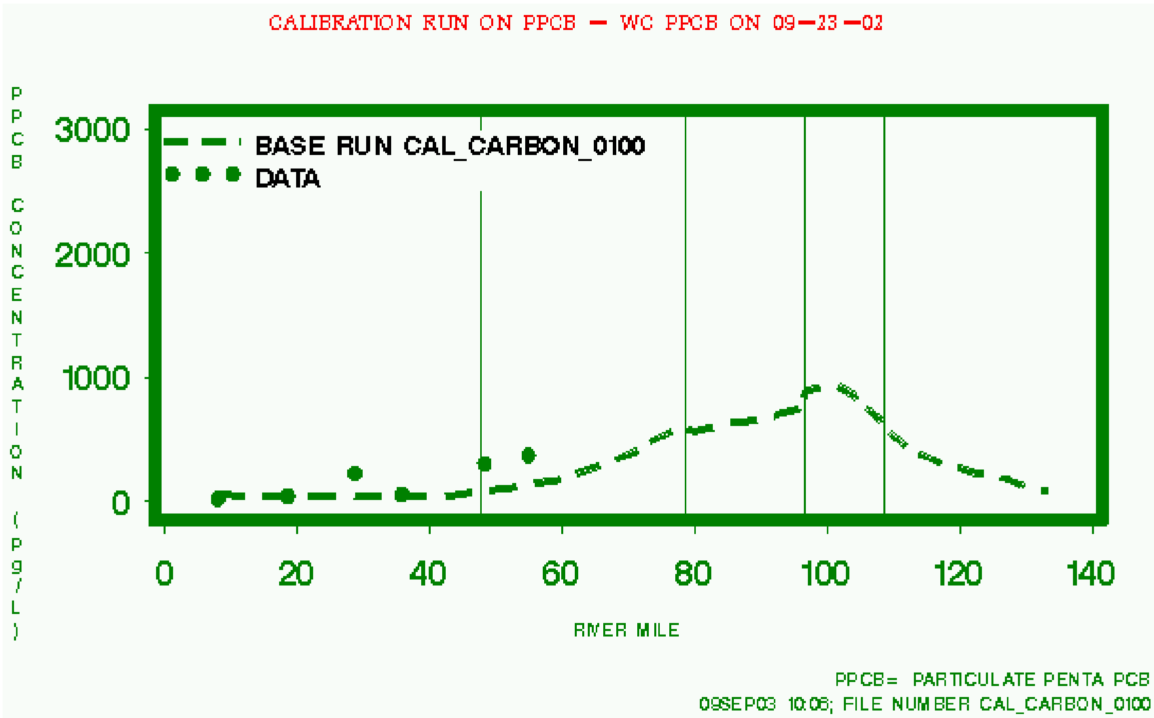


Figure 4.7 shows a comparison between simulated and observed particulate penta-PCB water column concentrations in the downbay portion of the estuary.

Figure 4.8 - Longitudinal Comparison of Simulated and Observed Particulate penta-PCB / g OC (R_1)

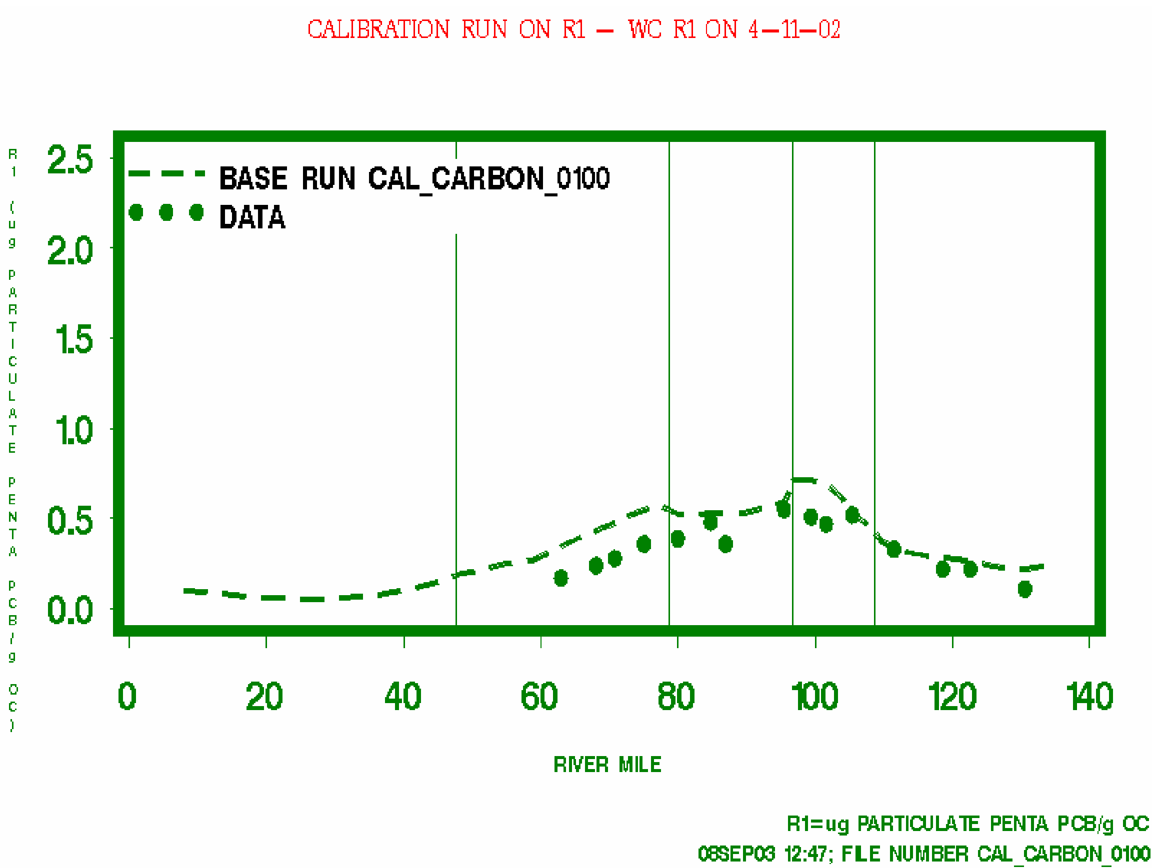
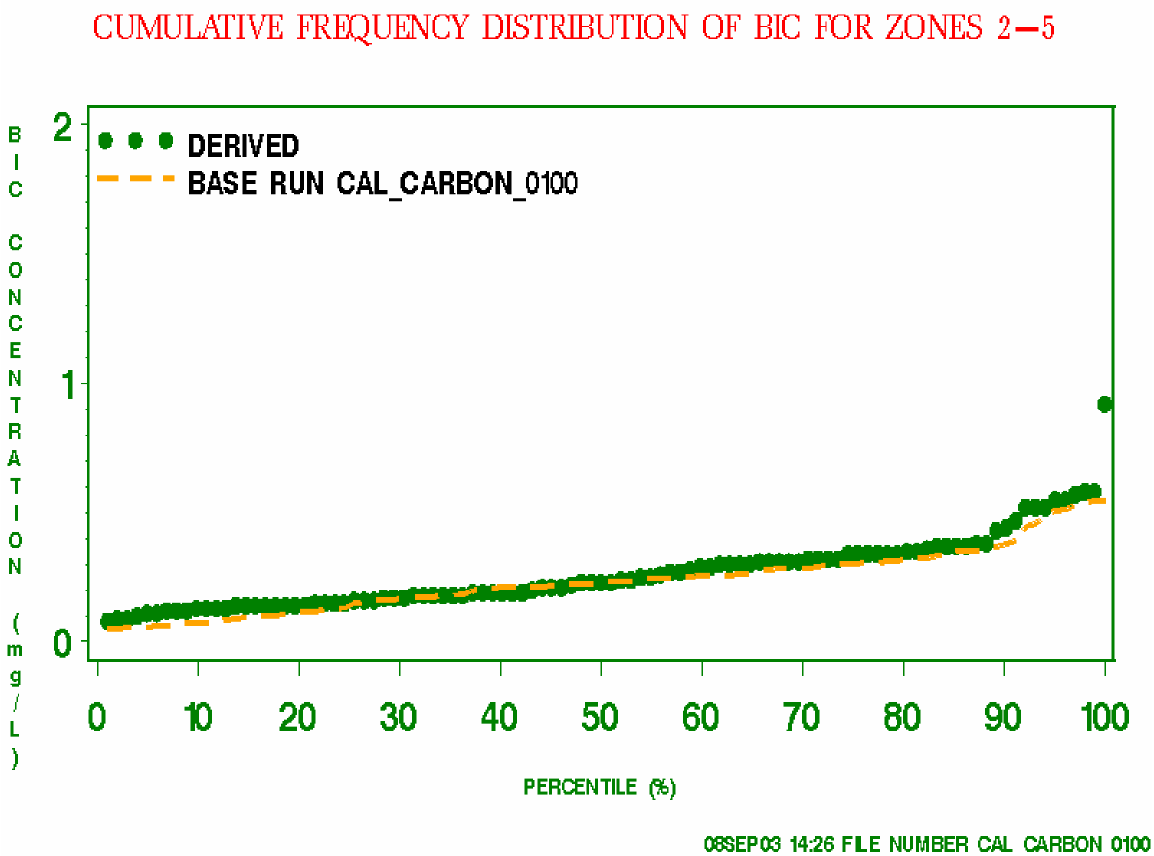


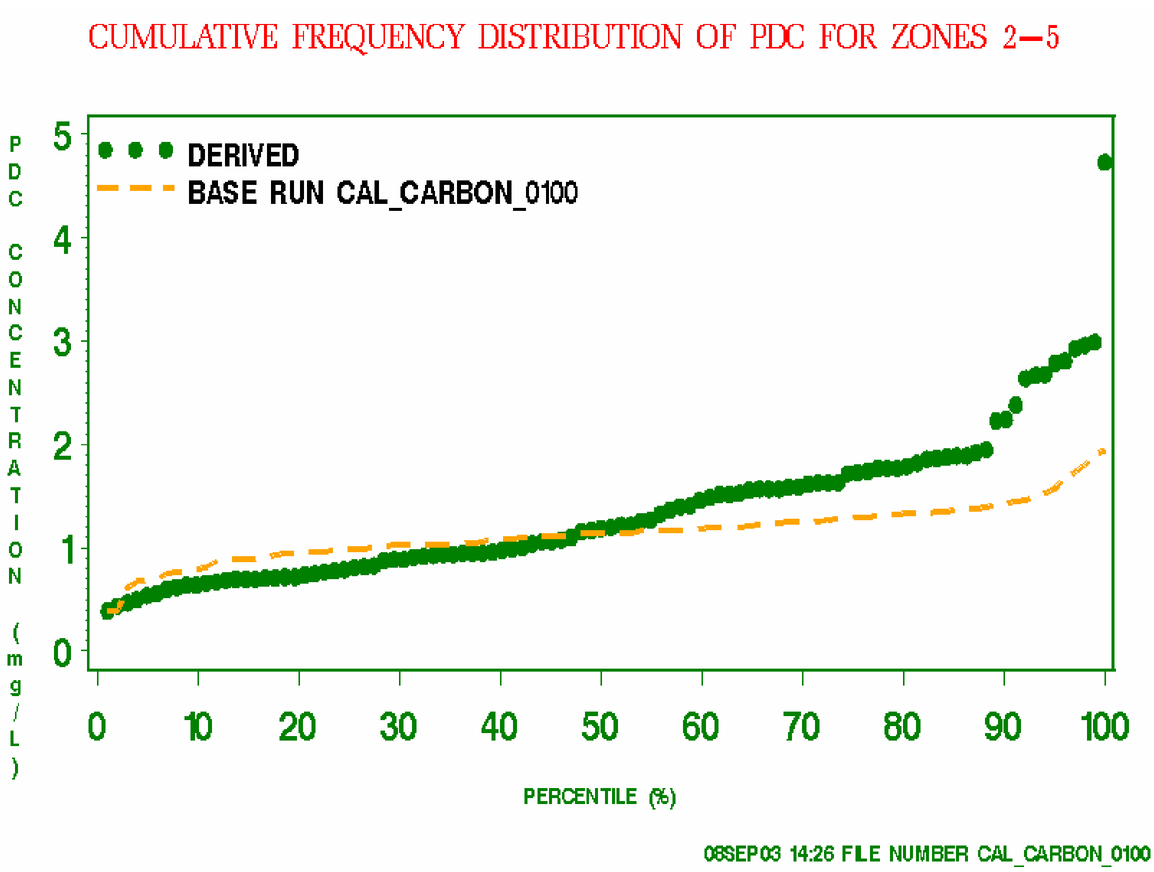
Figure 4.8 shows a comparison of simulated and observed carbon normalized particulate penta-PCB (R_1) water column concentrations. Note that carbon normalization improves the fit between simulated and observed values and more closely duplicates the structure seen in Zones 3 and 4.

Figure 4.9 - Comparison of Cumulative Frequency Distributions for Simulated and Derived BIC Concentrations



The cumulative frequency distribution comparison of simulated and derived BIC in Figure 4.9 shows that the model captures both the range and distribution of BIC water column concentrations. Distributions for Zones 2 through 5 are presented here because these Zones were the primary focus of the model calibration effort. Complete Zone 2-6 CFD plots are in the appendices.

Figure 4.10 - Comparison of Cumulative Frequency Distributions for Simulated and Derived PDC Concentrations



The cumulative frequency distribution comparison of simulated and derived PDC is shown in Figure 4.10. While the range and distribution generally agree and median concentrations agree, the comparison indicates some underprediction at higher concentrations, which relates to the previously mentioned underprection in Zone 5 (due to missing carbon load and/or the limitations of a 1D model for describing the effects of two-layer flow which lead to the formation of a so-called turbidity maximum zone), and slight overprediction at lower concentrations.

Figure 4.11 - Comparison of Cumulative Frequency Distributions for Simulated and Observed Particulate penta-PCB Concentrations

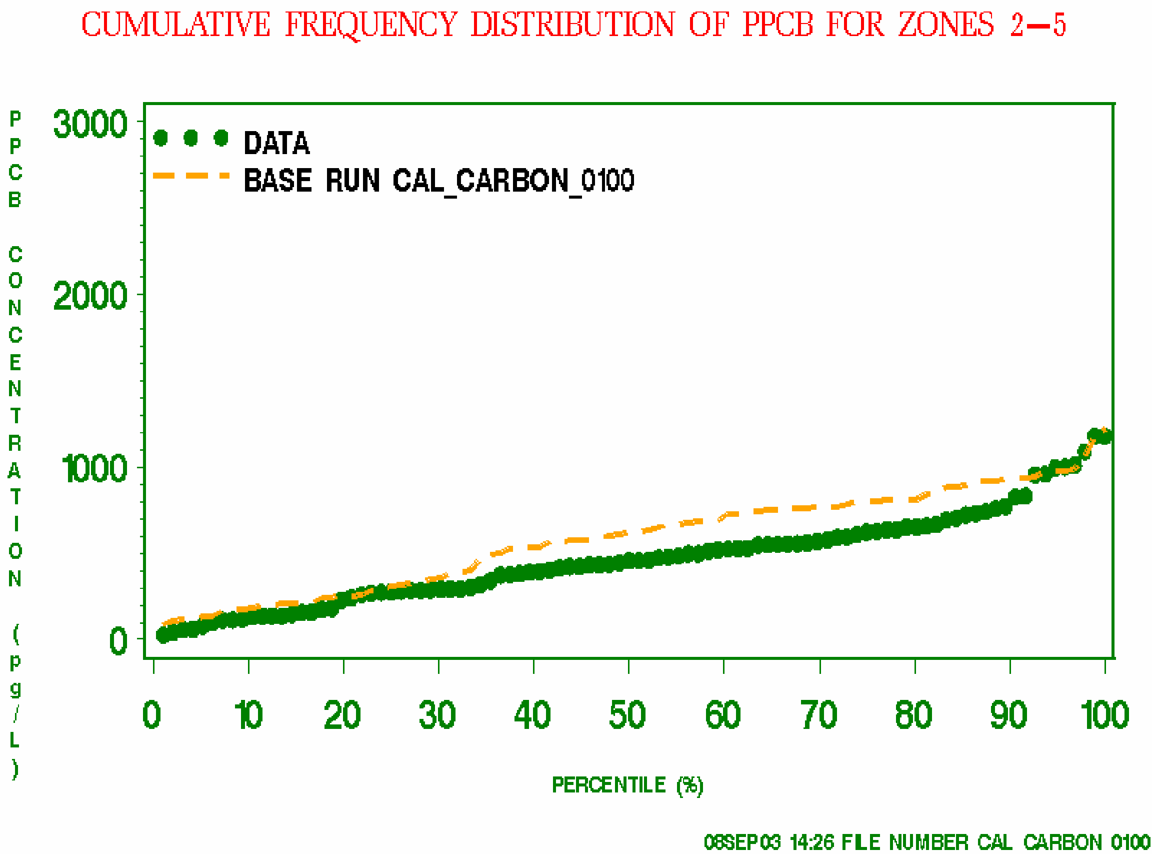


Figure 4.11 shows the cumulative frequency distribution comparison of simulated and observed particulate penta-PCB. This figure shows good agreement for the range and distribution of water column concentration values, with some slight overprediction near the median.

Figure 4.12 - Comparison of Cumulative Frequency Distributions for Simulated and Observed DDPCB Concentrations

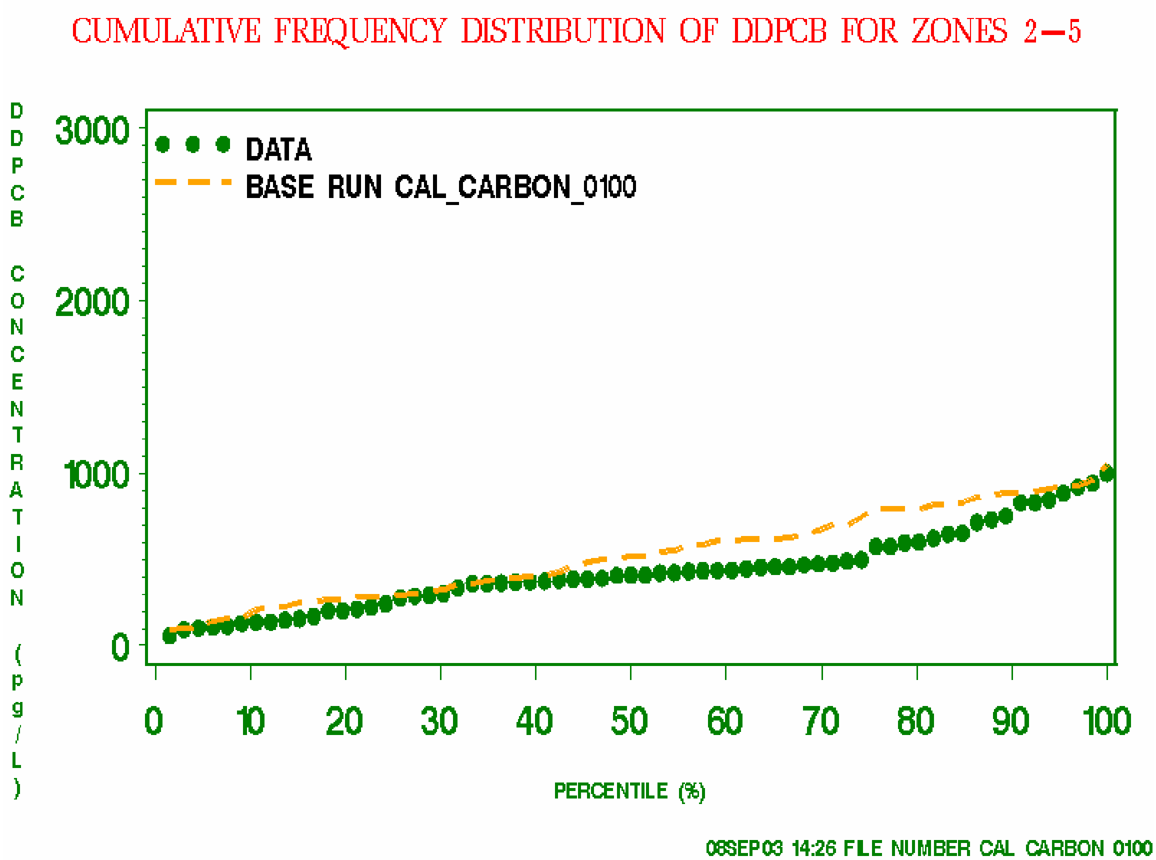
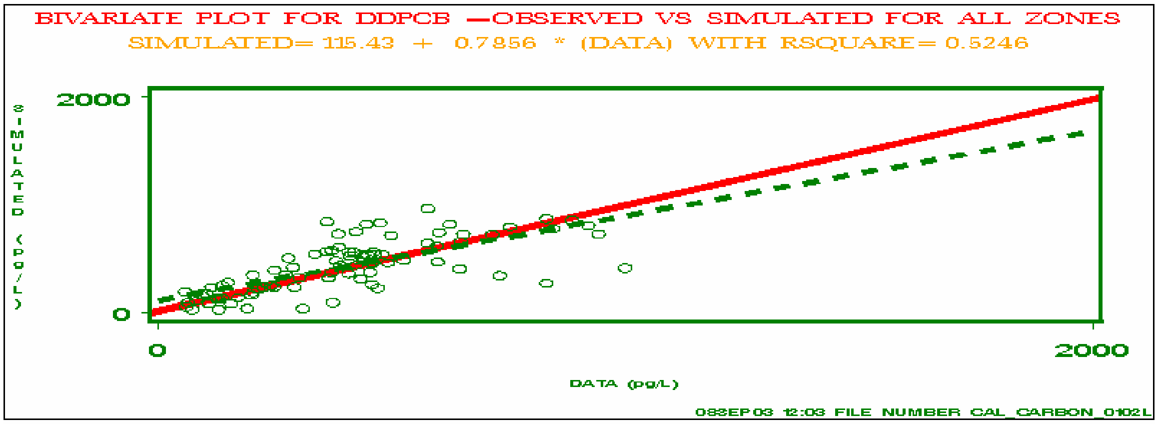
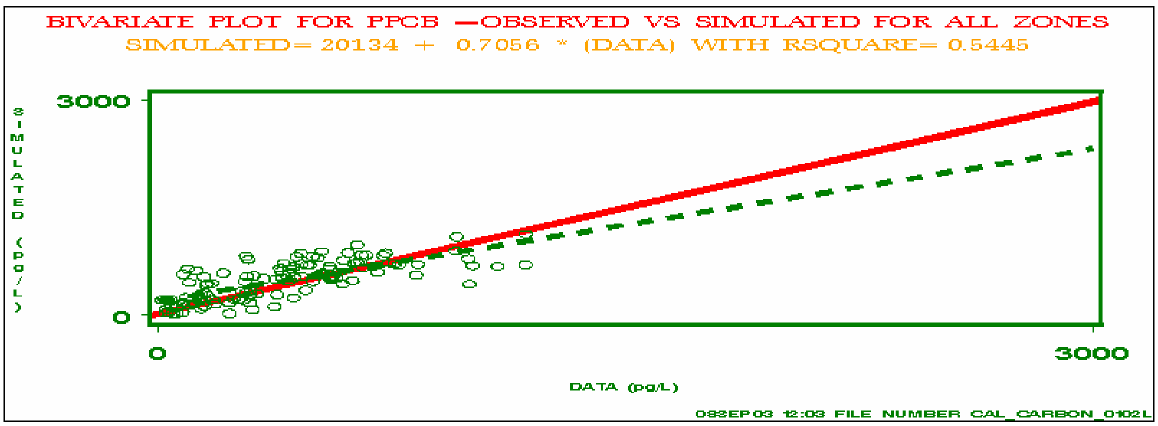


Figure 4.12 shows the cumulative frequency distribution comparison of simulated and observed truly dissolved + DOC-bound penta-PCB. This figure again shows good agreement for the range and distribution of water column concentration values, with some slight overprediction near the 75th percentile values.

Figure 4.13 - Comparison of Bivariate Plots for Simulated and Observed DDPCB and PPCB Concentrations





Finally, the bivariate plots shown in Figure 4.13 indicate good agreement between simulated and observed values of particulate and dissolved (as the sum of truly dissolved plus DOC-bound) penta-PCB for all available observation data sets. The R^2 values of 0.5246 for particulate penta-PCB and 0.5445 for dissolved penta-PCB, corresponding to correlation coefficients of 0.7243 and 0.7379 respectively, exceed EPA's recommended correlation coefficient acceptance criteria for water quality variables of 0.6 (EPA, 1990). These plots demonstrate good agreement and a low bias of the estimate in the region of the median concentration value, which is also the region around which the majority of observations are grouped. The slope and intercept of the lines suggest slight overprediction at low concentrations and the potential for underprediction at the high end of the concentration range.

5 Decadal Scale Consistency Check

5.1 Introduction

5.1.1 Background

Due to their hydrophobic nature, PCBs strongly adhere to, and are transported with the organic carbon fraction of solids. The sediment bed in aquatic systems has a high solids concentration and therefore it usually is a significant storage compartment for PCBs. PCBs are moved between the water column and sediment bed by various processes, including solids deposition and resuspension, and pore water diffusion. The result is that (a) the sediment bed acts to decrease the response time of the estuary to changes in forcing functions, and (b) the "legacy" PCBs presently in the sediment bed are a current source to the water column.

The sediment bed has a slow response time (compared to the water column), which makes it difficult to constrain the model parameters that determine the water column-sediment bed interaction using short-term simulations. The net accumulation of solids in the sediment, quantified as the burial rate, can be constrained using information from sediment cores dated using various tracers (e.g. ^{137}Cs), and dredging records. However, information on the net accumulation of sediment does not constrain other sediment parameters that affect the long-term behavior of PCBs: the intensity of interaction between the water column and sediment bed via solids deposition and resuspension, and pore water diffusion; and the effective size of the sediment bed reservoir determined by the mixed layer depth. As a result, various combinations of settling and resuspension velocities and mixed layer depths can produce an adequate fit to the current water column data and net burial rate.

To illustrate the buffering effect of the sediment bed and the effect of the sediment parameters, several "washout" simulations with various combinations of settling and resuspension velocities and mixed layer depths were performed. Either high settling (1 m/day) and the correspondingly appropriate resuspension velocities, or low settling (0.5 m/day) and the smaller resuspension velocities, denoted as high/low interaction were used. Also two sediment mixed layer depths: 5 cm and 10 cm (small/large reservoir) were employed. These depths were assigned by DRBC/LTI based on observed ^{137}Cs and PCB profiles in sediment cores. The simulations were started at present conditions and all forcing functions (e.g. point source loads, tributaries, atmospheric gas phase concentration, etc.) were set to zero. It should be pointed out that this is not a realistic scenario because it is impossible to completely eliminate all inputs to the estuary. The results are presented in Figure 5.1. As a point of comparison, the present total PCB water quality criterion of 44 pg/L is also presented. Without sediment bed interaction the estuary would reach the water quality criterion in a very short time (~2 months–the almost vertical line in Figure 5.1). However, with sediment bed interaction the response time is much longer and, depending on the sediment transport scenario, it would take 15-40 years to reach the criterion (for this future zero-load scenario).

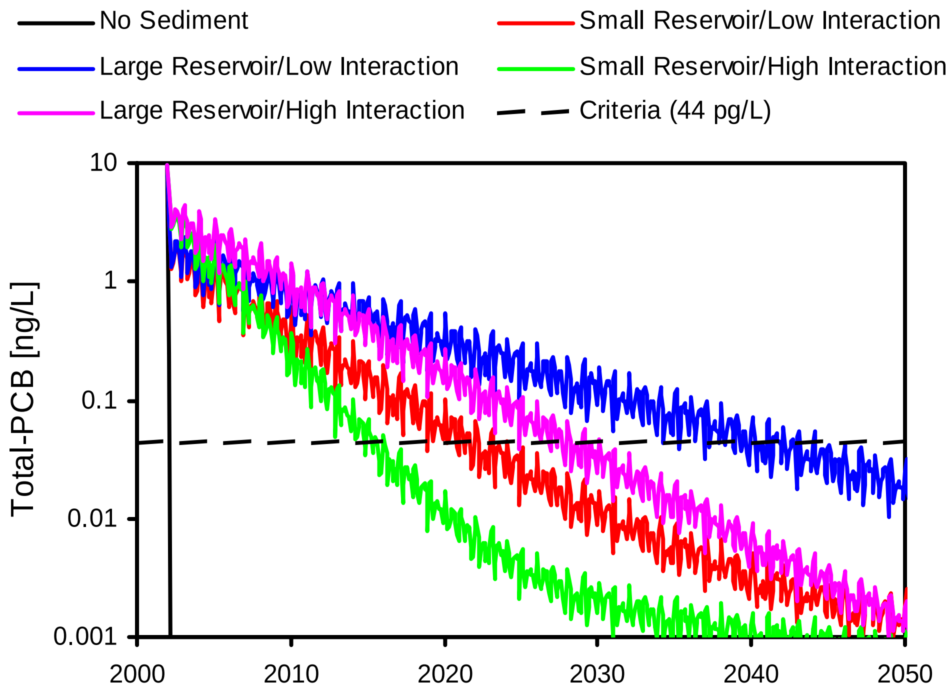


Figure 5.1 – Washout simulations for various sediment transport scenarios

Results are for model segment 44 near the Schuylkill River in Zone 4.

The washout simulations also illustrate that the PCBs presently in the sediment bed are a current source to the water column. At the beginning of the simulations, after the water column has equilibrated with the sediment bed (~2 months), the water column concentration is about 3 ng/L (depending on the scenario), which is close to the ambient concentrations currently measured. With all the loads set to zero, sediment interaction results in a water column concentration that is close to present levels.

To further illustrate the contribution of the PCBs currently in the sediment bed to the PCB concentration in the water column another diagnostic simulation was performed. The short-term simulation was run with initial PCB concentrations in the sediment bed set to zero. For this simulation the "large reservoir/high interaction" sediment transport scenario, which is the final one selected for the short-term simulation, is used. The results of the simulation, presented in Figure 5.2, show that about half of the PCB mass in the water column can be attributed to the PCBs currently in the sediment bed. It should be noted that the sediment bed is also a sink of PCBs, and depending on the time and location, the sediment bed can be a net source or sink.

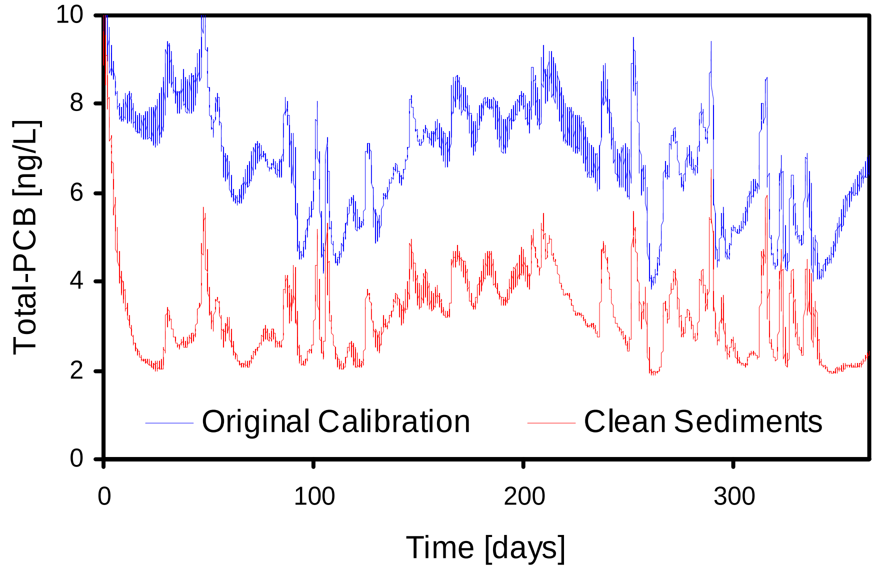


Figure 5.2 – Short-term simulation with and without PCBs in the sediment
Results are for model segment 44 near the Schuylkill River in Zone 4.

One way to constrain the sediment parameters (settling and resuspension velocities, mixed layer depth) is to perform a long-term simulation of a tracer for which the historical loading is known, for example ^{137}Cs (Lower Hudson River, Thomann et al., 1989; Green Bay, DePinto et al., 1993). Another approach is to reconstruct the historical loading of PCBs and to check the model's performance using this loading. This approach is adopted for the Delaware Estuary PCB model.

5.1.2 Objective and scope

Due to the importance of the sediment bed in influencing the fate and transport of PCBs in the estuary, the PCB Model Expert Panel recommended DRBC perform a long-term (decadal scale) simulation. Significant time constraints prevented DRBC from diverting attention from the short-term simulation. In order to contribute to the overall TMDL process, the Delaware Estuary TMDL Coalition agreed to fund this analysis and retained HydroQual to perform this task. The work consisted of using the DRBC model as constructed by DRBC and performing long-term simulations. No other parts of the DRBC model were evaluated as part of this effort.

The purpose of this section is to present the results of the long-term simulation of PCBs in the Delaware Estuary. The objective of the analysis was to determine if the long-term behavior of the model is consistent with the available data. The strategy used was to simulate the period from the beginning of PCB production to the present. That is, to perform a hindcast, and compare the model computed PCB concentrations to historical and contemporary data. The remainder of this section documents the data sources

(Section 5.2), PCB loading development (Section 5.3), hindcast results (Section 5.4), and the conclusions and recommendations (Section 5.5).

5.2 Data Sources

To evaluate the model's long-term behavior requires historical PCB data. An extensive data search for historical PCB concentrations in various media (water column, sediment bed, fish and birds) was performed. All data found were included. A special effort was made to locate data as far into the past as possible since a long time span is often required to identify a time trend when other sources of unaccounted variability are present, such as spatial variations where samples were taken. The data sources are summarized in Table 5.1, and the data are presented and discussed along with the model results in Section 5.4.

Table 5.1: Sources of Historical PCB data

Source	Year	N	D
Water column			
Crump-Wiesner et al. (1973)	71-72	11	3
Kurtz (1978), PADER (1980)	74-75	10	3
USACOE (unknown date)	~80	11	2
Collier (1980)	80	4	0
Stamer et al. (1985)	79-80	12	10
Taylor (1996)	95	1	0
Versar (1999)	98	4	4
Versar (2000)	99	4	4
DRBC (2002)	01	12	12
Sediment bed			
Crump-Wiesner et al. (1973)	71-72	12	10
PADER (1980)	76-77	37	16
Collier (1980)	80	10	5
USACOE (unknown date)	~80	36	7
USACOE (1981)	81	4	0
Hochreiter (1982)	79-81	18	17
NOAA (2003)	86-97	46	46
USACOE (1997, 2003)	91,92,94	84	2
Costa and Sauer (1994)	93	16	16
Block (1991)	89	4	0
Hardy et al. (1995)	85-87	40	25
DRBC (1994)	91	22	0
Taylor (1996)	95	17	7
Burton (1997)	96	15	15
McCoy et al. (2002)	97	64	64
DeLuca et al. (1999)	98-00	42	9

Table 5.1: Sources of Historical PCB data (*continued*)

Source	Year	N	D
Sommerfield and Madsen (2003), Eisenreich (2003)	48-01	27	27
EPA (2002a)	81-93	54	43
DRBC (2002)	01	51	51
Fish			
Greene (2002)	69-00		
Birds			
Clark et al. (2001)	98	6	6
Steidl et al. (1991)	89	7	7
Rattner et al. (2000)	97	15	15

N = number of samples; D = number of detects.

Due to different sampling and analytical techniques (e.g. packed vs. capillary column) the quality of historical contamination data is generally uncertain. An effort was made to quantify the accuracy of the historical data. In 1977 and 1979 White Perch collected from Zone 2 were analyzed using packed column Aroclor analysis techniques. The results are presented in Figure 5.3. Portions of the fish fillet were archived (frozen) and re-analyzed in 2003 using modern capillary column congener techniques. The total PCB concentrations computed by summing the Aroclors from the historical analysis and congeners from the contemporary analysis differ by 14% and 20% for the 1977 and 1979 fish, respectively, and no bias is evident. Although, this provides some reassurance in the accuracy of the historical data, it should be noted that these results are not necessarily representative of all historical data and larger errors and biases could be present for data in other media.

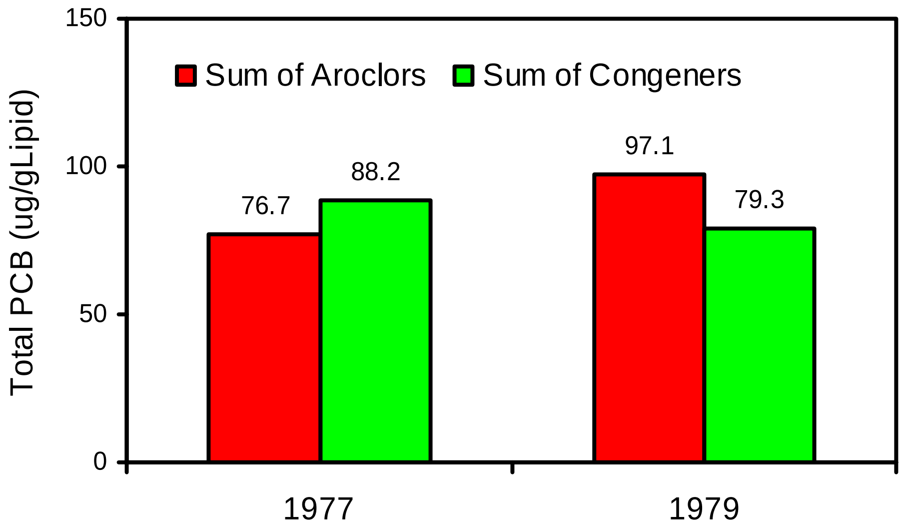


Figure 5.3 – Total PCB concentration in White Perch collected from Zone 2
The same two fish were analyzed in 1977 and 1979 using packed column Aroclor analysis and in 2003 using capillary column congener analysis.

5.3 PCB Loading Development

5.3.1 Strategy

The hindcast simulations are started in 1930, the approximate beginning of commercial production of PCBs (see Figure 5.4a), and ended in 2002, the time of the short-term simulation. This required developing historical time trends for PCB loads (point and non-point sources) and boundary concentrations (Delaware River at Trenton, Schuylkill River at Philadelphia, other tributaries, open boundaries at the Atlantic Ocean and C&D Canal, atmospheric boundary conditions). A back-scaling methodology is used to develop these inputs. This consists of developing a time trend of historical PCB forcing functions using various sources as discussed below. The PCB forcing functions for the hindcast are constructed by scaling the time trend using the present day values that are part of the short-term simulation. For example, the input associated with the Schuylkill River is assigned an average penta-PCB concentration of 1.1 ng/L in the short-term simulation. If the ratio of loads from 1970 to 2002 in the loading trend is 200, then a value of 1.1 x 200 = 220 ng/L is used for the Schuylkill River in 1970.

The loading trend is applied uniformly to all PCB forcing functions: e.g. point sources, open boundary concentrations, atmospheric gas phase concentrations, assuming they all followed the same historical time trend. Although this might not be a good assumption for some forcing functions, and evidence presented below suggests that this is the case for the Atlantic Ocean boundary condition, it greatly simplifies the analysis and facilitates the interpretation of the results.

There are two sources of uncertainty in the historical loading sequence constructed using the back-scaling methodology. The first is the shape of long-term loading time trend itself. The second is the current loadings, because the historical loadings are directly proportional to them. This means that any errors in the current loadings translate directly into errors in the historical loadings. Since there are large uncertainties in the current loadings there are also large uncertainties in the historical loadings.

Other, non-PCB, forcing functions: the hydrodynamic transport and organic carbon fate and transport, were cycled using the time series for the period 2/1/2002-1/31/2003. That is, these time series were repeated for each year in the long-term simulation. This period was identified by DRBC as a typical hydrologic year and therefore does not account for any inter-annual episodic events (e.g. hurricane, 50-year flood). Also, by cycling the organic carbon forcing functions the simulation does not account for any long-term changes in the organic carbon discharge from municipal wastewater treatment plants and non-point sources (erosion control practices).

To develop the historical forcing functions several trends were considered. Some trends were rejected after initial investigation of the loadings that resulted after back-scaling for various reasons: They produced loading trends inconsistent with the magnitude of PCBs produced during the simulation period. They produced a peak loading at a time inconsistent with the dated core data. Based on the ^{137}Cs dated core (PC-15, Woodbury Creek) it is known that the peak concentration in the estuary occurred at approximately 1970. Therefore, any loading trend would have to peak at approximately that time as well. Two loading trends were selected for simulation: one based on the estimated US penta-PCB air emission, and one based on the estimated Lower Hudson River total PCB emission, as discussed in the following sections.

5.3.2 US air penta-PCB emission trend (“Air Trend”)

An historical (1930-2000) emission inventory for 22 PCB congeners and 113 countries was developed by Breivik et al. (2002a,b). Briefly, the methodology consisted of estimating production and consumption (production + import – export) for each country. The consumption was divided amongst various usage categories (open, small capacitors, nominally closed, closed). Emissions then occur directly as a result of the usage (i.e. open usage), accidental release, or after the lifetime of the usage category (e.g. small capacitors) when it is disposed of in some way (landfills, open burning, waste incineration, destruction). The purpose of the model by Breivik et al. was to produce input to a global PCB fate and transport model (Globo-POP, Wania and Daly, 2002). On a global scale, transport via the atmosphere is most important and because of that Breivik et al. estimated emissions to air only. Figure 5.4b shows the time trend they developed.

Breivik et al. developed three emission trends designated as low, mid and high based on the uncertainties in the model input parameters (e.g. lifetime of small capacitors). The absolute magnitude of the estimates vary by up to three orders of magnitude and the time trends have different shapes as well. Differences in the absolute magnitude are not important in this analysis, because the absolute magnitude is normalized out in the back-scaling procedure. In other words, if the emission rate for every year were higher by a factor of 10 (e.g. 170 instead of 17 t/year in 1970, Figure 5.4b) the output of this analysis would be identical. However, differences in the shape of the time trend are important in this analysis. As an example, if the emission rate for just 2002 were higher by a factor of 10 (0.85 instead of 0.085 t/year, Figure 5.4b) then the mass discharged in the hindcast simulation would change by a factor of 10 for every year (except 2002). Here we use the mid estimate of Breivik et al. as being representative of their best estimate. The analysis by Breivik et al. was limited to 22 congeners, 6 of which are penta-PCBs. Since the DRBC model is for penta-PCBs we use the sum of the 6 penta-PCB congeners. This assumes the time trend of the sum of the 6 penta-PCB congeners is representative of the time trend of the sum of all penta-PCB congeners.

In this study the Breivik et al. trend is used for emissions to the Delaware Estuary. Although air and water are different emission pathways, it is reasonable to assume that their time trends are similar. Consider, for example, the disposal of capacitors to landfills. As emissions to the air occur by volatilization, emissions to water occur by rainfall runoff. Since both are related to the same landfill source, it is not unreasonable to assume that the time trend of PCBs attributable to that source would be the same. However, some emission scenarios, like fires, are clearly different and a future analysis might refine the work of Breivik et al. to estimate emissions to water. It should be emphasized that it is not assumed that the air emission estimate from Breivik et al. is applicable to the water emission to the Delaware Estuary, but rather that the time trends have the same shape. The Breivik et al emission time trend ended in 2000. The trend was extended from 2000 to 2002 using an exponential curve fit (see Figure 5.4b).

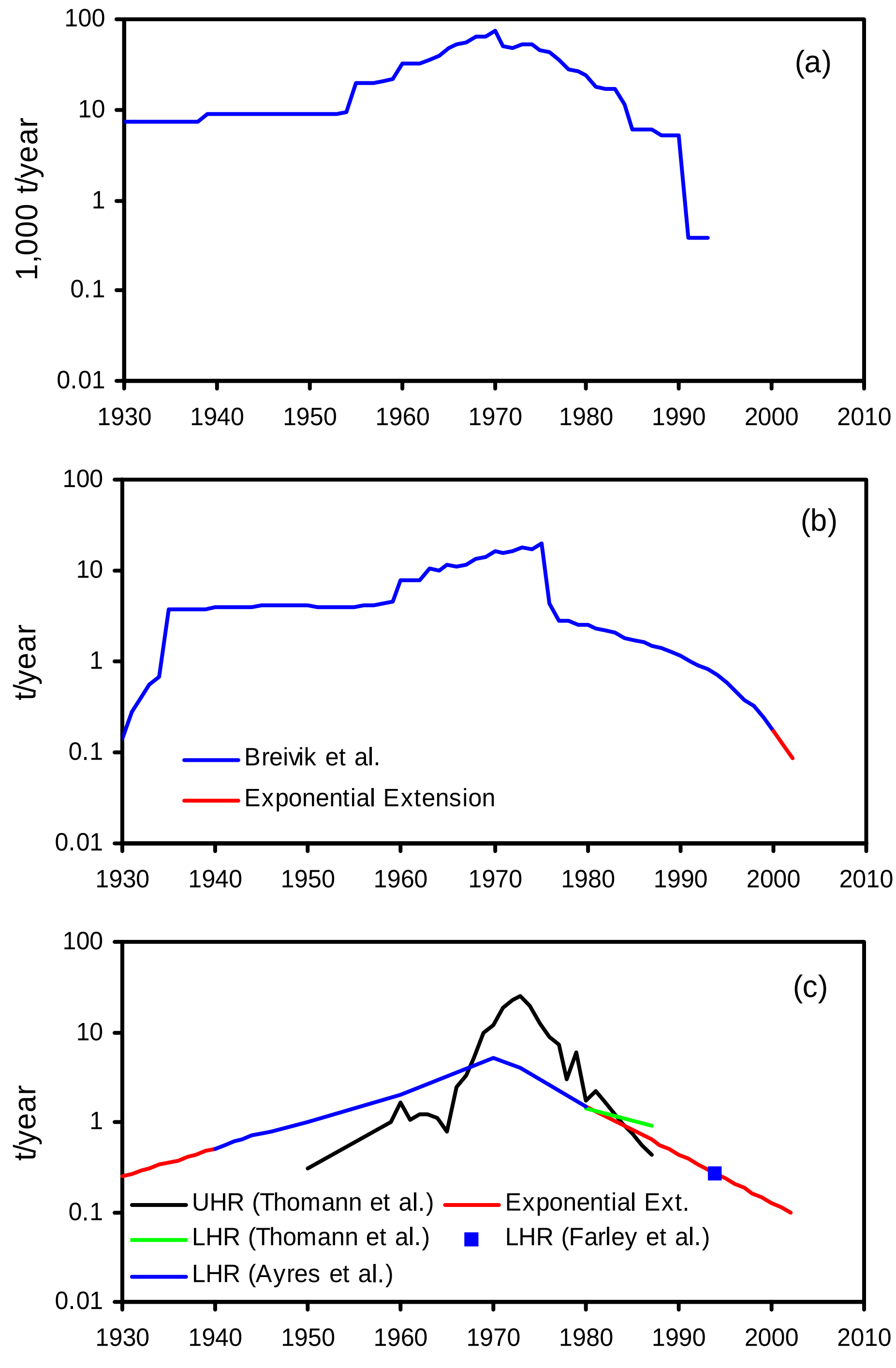


Figure 5.4 – Production and Emission Trends

(a) Global total PCB production (from Breivik et al. 2002a). (b) US penta-PCB air emission (sum of 6 congeners, mid estimate from Breivik et al. 2002b) and exponential extension to 2002. (c) Hudson River load estimates (UHR = Upper Hudson River, LHR = Lower Hudson River, Ayres et al. 1985, Thomann et al. 1989, Farley et al. 1999).

5.3.3 Lower Hudson River total-PCB emission trend ("Hudson Trend")

Thomann et al. (1989) performed a historical simulation of PCB fate and transport in the Lower Hudson River. PCB mass entering the Lower Hudson River can be broken down into that from the Upper Hudson River, which is significantly influenced by discharges from two General Electric (GE) plants, and that from other sources. The following discussion refers to inputs entering the Lower Hudson River from sources other than the Upper Hudson River. Thomann et al. developed a loading function using a similar strategy as done here. Using various information sources they estimated the PCB loads for one year (1980) and then applied the time trend of historical PCB discharges developed by Ayres et al. (1985) (Figure 5.4c). The loads calculated by Thomann et al. are close to the estimates of Ayres et al. (1.46 vs. 1.5 t/yr in 1980). To extend the trend from the end of the Ayres et al. estimate (1980), to the end of their model period (1987) Thomann et al. applied the rate of decrease of PCBs in striped bass. The extension is shown in Figure 5.4c. In a subsequent analysis Farley et al. (1999) estimated the PCB loads to the Lower Hudson River for 1994. This analysis was done based on measurements, independently of the Thomann et al. extension. That estimate indicates a significantly faster rate of decrease from 1980 than estimated by Thomann et al. This is not surprising as it is expected that the decrease in striped bass lags the decrease in loads. The load estimate of Farley et al. corresponds to an exponential decrease from 1980 at about the same rate as the decrease from 1970 to 1980 in the Ayres et al. estimate (Figure 5.4c). The trend used in this study consists of the Ayres et al. estimate, with extensions for the periods 1930-1940 and 1980-2002 (Figure 5.4c). The extension for 1930-1940 was assumed to be exponential based on the rate of increase from 1940 to 1950 in the Ayres et al. estimate. For the extension for 1980-2002 an exponential decreases was assumed based on the rate of decrease from the 1980 Ayres et al. to the 1994 Farley et al. estimates. The rate of decrease thus obtained is similar to the rate of decrease from 1970 to 1980 in the Ayres et al. estimate.

5.3.4 Trend evaluation

Only limited data are available to evaluate the resulting loading trends. Water column PCB concentrations from two tributaries (Schuylkill River and Rancocas Creek) are overlaid with the loading trends in Figure 5.5a. The data were scaled so that the recent data (~2000) are in agreement with the loadings trends. Note that since data are not necessarily available for 2002 this adjustment involved some judgment. If the loading trends are appropriate for those tributaries then the historical data (1970-1980) should be close to the loading trends as well. The same test was done for PCB concentrations in sludges from municipal wastewater treatment plants (Figure 5.5b). The comparison suggests that the loading trends might underestimate the peak concentration in the Schuylkill River. The comparison for Rancocas Creek is good, with the data point in 1971 lying between the two loading trends. The trend of PCB concentrations in sludges observed is in reasonable agreement with the loadings trends. It should be pointed out that these comparisons only provide support for portions of the historical time trends (i.e. the marked decline from the 1970s to ~2000 for the tributaries, the marked decline from the 1950s to 1990s for the sludge). Other parts of the time trends (e.g. continued decrease during the 1990s in the tributaries or sludge) cannot be evaluated in this manner due to the lack of data.

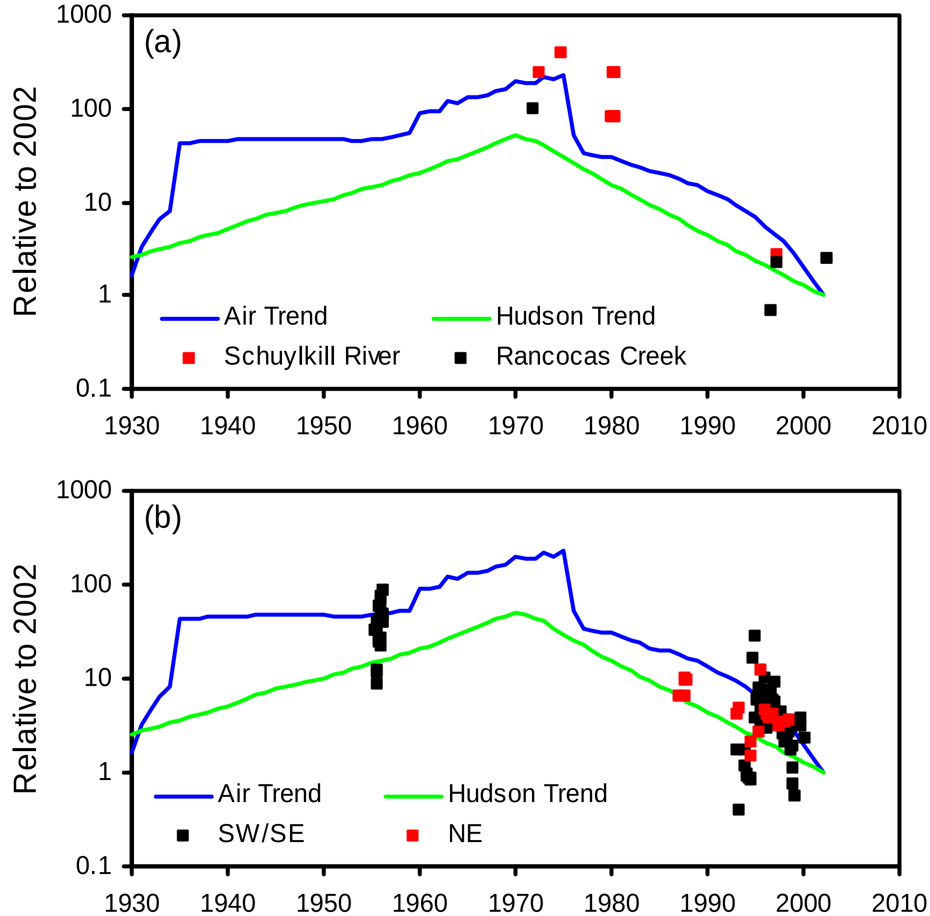


Figure 5.5 – Comparison of loadings trends with (a) tributary concentrations and (b) municipal wastewater treatment plant sludge concentrations

SW/SE and NE refer to different treatment plants of the Philadelphia Water Department. Data were provided by D. Blair (personal communication).

Another check is to compare the total mass discharged to the Delaware Estuary to other water bodies. The total PCB mass discharged to the estuary calculated by back-scaling and integrating the loading trends are compared to other mass estimates in Table 5.2. This check is useful, because the present analysis is not constrained by the total mass discharged. Some time trends produced a total PCB mass in excess of the global production and this check served as a basis for dismissing those trends. The total global production exceeds 1 million tons of which approximately 650,000 tons were produced in the US. The US air emissions were approximately 8,500 tons. Discharges to major waterbodies (Hudson and Fox Rivers) are in the range of approximately 100 to 600 tons. The two trends used for the Delaware Estuary are in the same range suggesting the time trends are not unreasonable.

Table 5.2: PCB Mass Inventories

Description	Total PCB (tons)
Production	
Global (a)	1,324,131
US (a)	641,700
Emissions	
Global to air (a)	18,538
US to air (a)	8,509
Upper Hudson River (GE plants) (b)	95-590
Lower Hudson River (c)	78
Lower Fox River (paper mills) (d)	314
Delaware Estuary	
"Air Trend"	512
"Hudson Trend"	128

(a) Breivik et al. (2002), (b) EPA (2002b), (c) 1946-1987, excluding Upper Hudson River, Thomann et al. (1989), (d) WDNR (1999).

5.4 Hindcast Results

This section presents the results of the hindcast simulations. For many historical data only total PCB concentrations are available and to allow for a comparison the model computed penta-PCB concentrations were multiplied by a factor of 4. This approximates the ratio of total PCBs to penta-PCBs found in the present forcing functions and present and historical (dated core) ambient data. It should be pointed out that the ratio of total to penta-PCBs can vary significantly (3 to 400 in the DRBC surficial sediment data). When model results are presented by zone they correspond to the average of the model segments for the mainstem estuary (e.g. segments 49, 51, 52, 53, 55, 56, 58 for Zone 3). Data reported as below detection limit are not included in the figures. When only a subset of Aroclors or congeners analyzed for were detected the data point is plotted at the logarithmic midpoint of the range obtained by setting non-detects to zero and the detection limit (see example in Section 5.4.1).

Various combinations of sediment transport parameters (settling and resuspension velocities, mixed layer depth, see Figure 5.1) were simulated. There are significant differences for the various scenarios. However, without more confidence in the historical data and historical and current forcing functions the hindcast simulations are unable to constrain the sediment parameters further. Here only the results of the final sediment transport scenario (high interaction/large reservoir) are presented, consistent with the presentation of the short-term simulation results. The results for the other three simulations are presented in Appendix G.

5.4.1 Historical water column data

The historical water column data for Zone 3 are presented in Figure 5.6. Data in other zones are insufficient for a useful model-data comparison. The 1980 data point represents two samples. Each sample was analyzed for 7 Aroclor mixtures (e.g. Aroclor1242). One Aroclor mixture was detected and quantified as "1-9 μg/l" and 6 Aroclor mixtures were reported as not detected (USACOE, unknown date). Based on the reported values, the estimated total PCB concentration of the samples ranges from 1,000 (1×1,000+6×0) to 15,000 (1×9,000+6×1,000) ng/L. This data point is plotted at the logarithmic midpoint of that range (4,000 ng/L) in Figure 5.6. The model results for the Air Trend fall within the range of data (assuming the 1980 data are representative of actual conditions). The results for the Hudson Trend are below the data in the late 1970s. Both trends are in good agreement with the contemporary data in 2001.

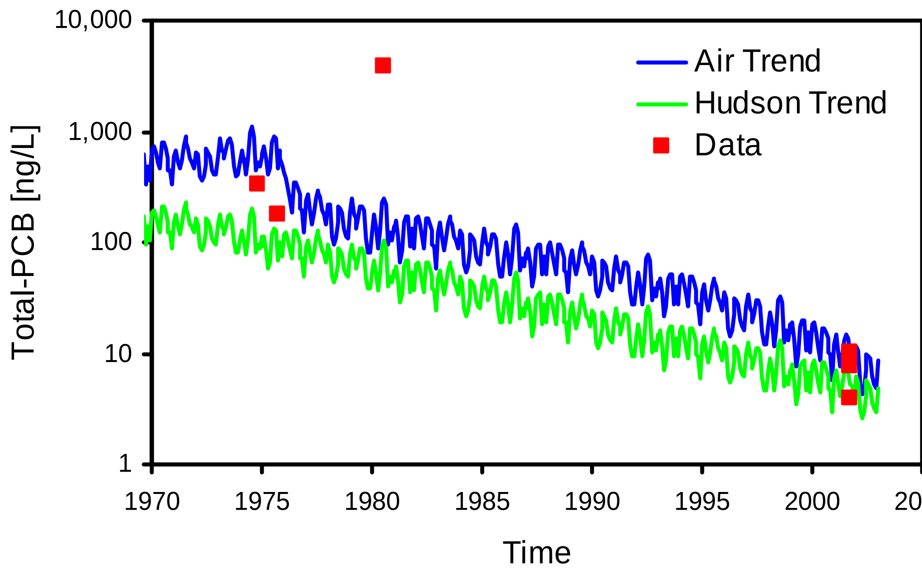


Figure 5.6 – Historical water column total-PCB concentrations in Zone 3

5.4.2 Historical sediment data

Historical sediment concentrations for Zones 2- 6 are presented in Figure 5.7. The data are highly variable, presumably a result of high spatial variability. Here all samples were lumped by zone. It is possible that a more careful analysis that accounts for differences in sample location (e.g. main channel, nearshore, near tributary mouths, etc.) would reduce some of that variability. The data in all zones are relatively constant in time and a trend of decreasing concentrations is not evident. By comparison the model results for both loading trends are on the high end of the data and decrease in time. Thus the model is not in agreement with the long-term trend seen in the sediment data. This could be the result of error(s) in the model, forcing functions and/or data.

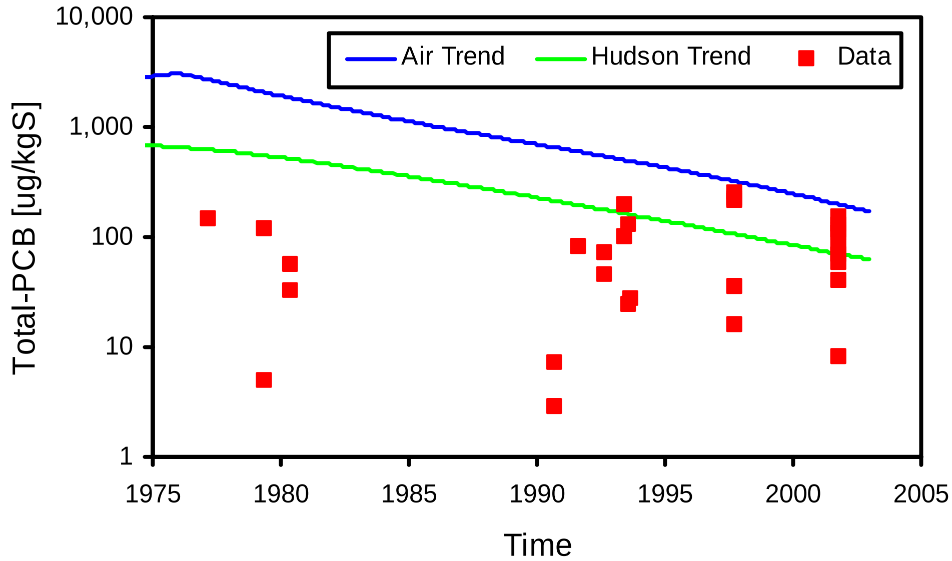


Figure 5.7(a) – Historical sediment bed total-PCB concentrations in Zone 2. Model results are average of layers 1 and 2

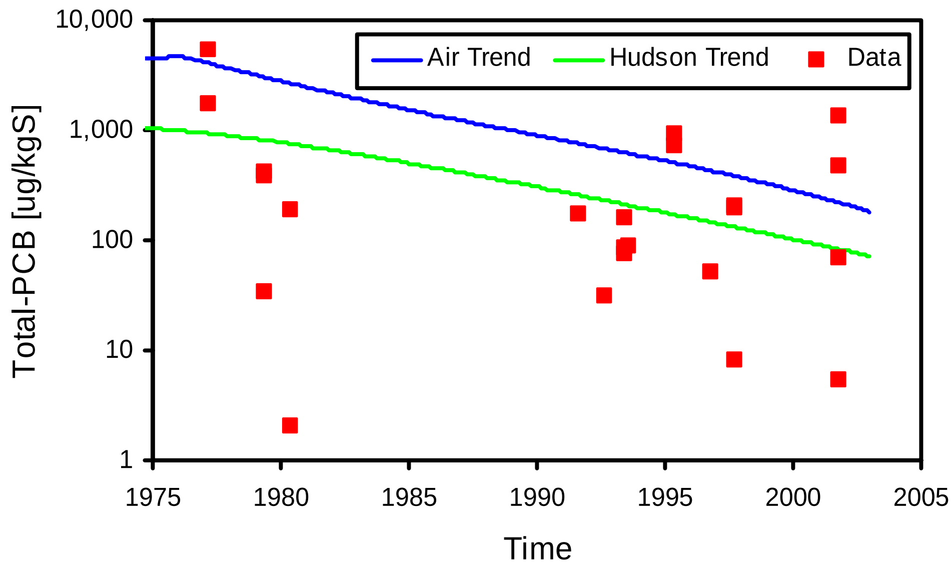


Figure 5.7(b) – Historical sediment bed total-PCB concentrations in Zone 3. Model results are average of layers 1 and 2

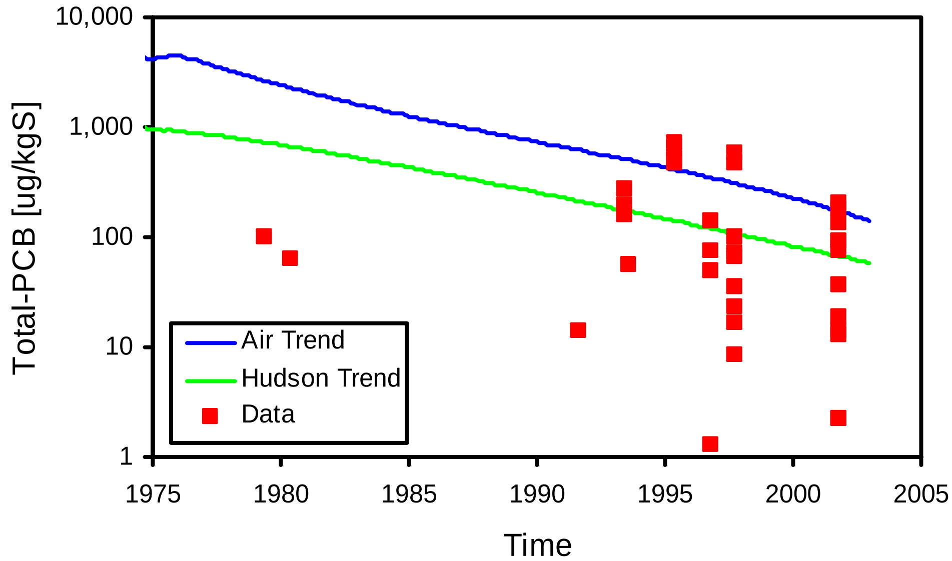


Figure 5.7(c) – Historical sediment bed total-PCB concentrations in Zone 4. Model results are average of layers 1 and 2

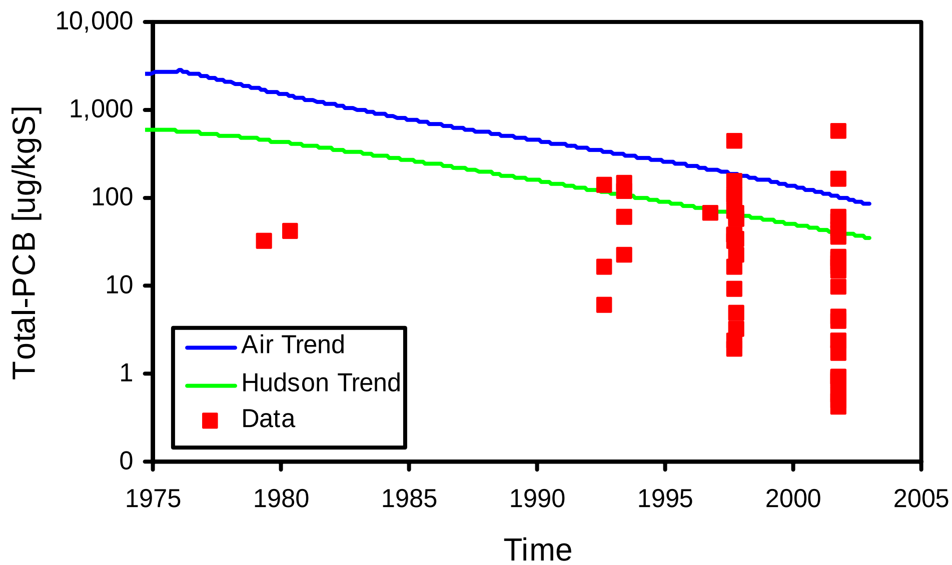


Figure 5.7(d) – Historical sediment bed total-PCB concentrations in Zone 5. Model results are average of layers 1 and 2

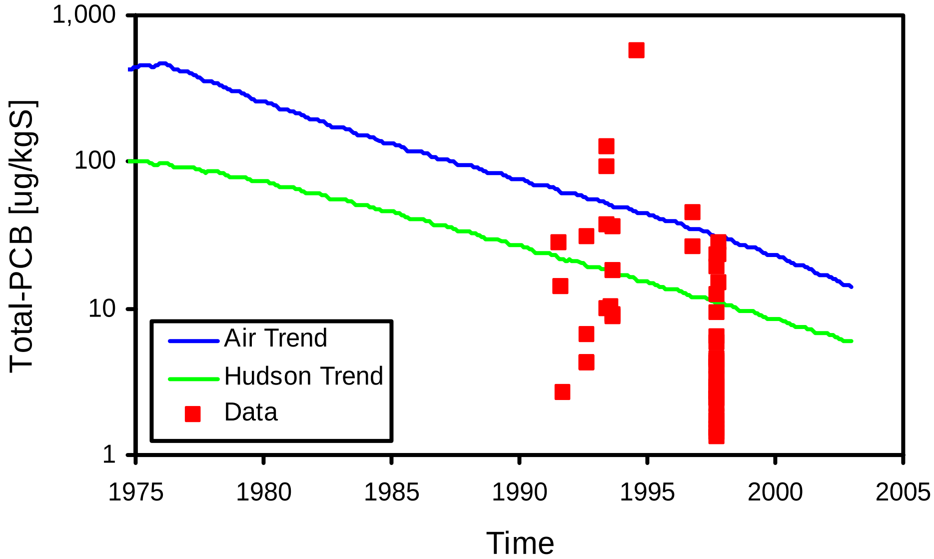


Figure 5.7(e) – Historical sediment bed total-PCB concentrations in Zone 6. Model results are average of layers 1 and 2

5.4.3 Historical fish data

Observed PCB concentrations in fish, compiled by Greene (2002), are presented in Figure 5.8 for Zones 2-6. For this comparison fillet and whole body results are not differentiated and when no lipid data are available it is assumed the lipid content is the average of the samples in the database (fillet = 2.7%, whole body = 6.8%, White Perch). Those data points are represented by different symbols on the plots.

The model does not include a fish compartment and a direct model-data comparison is therefore not possible. Fish concentrations on a μg/gLipid basis are compared to water column and sediment bed concentrations on a μg/gOC basis. The validity of this method depends on the assumptions that the partitioning of PCBs between water and organic carbon, and water and fish lipid is similar. For hydrophobic chemicals (like PCBs), this is known to be the case (Di Toro et al., 2000). The comparison is complicated by biomagnification, however, which will tend to increase the fish concentrations relative to the water column and sediment concentrations. Also, it is expected that the time trend of fish tissue concentration lags that of the water column and/or sediment bed concentrations, because it takes some time for the PCBs to move up the food chain. Whether the fish concentrations should reflect the water column or sediment bed concentration depends on the source of PCBs for the fish. The reasoning for presenting model results for both compartments is that depending on the base of the food web (benthic or pelagic) the fish concentration should equilibrate with the water column or sediment bed or some combination of them. The data shown in Figure 5.8 are for White Perch whose feeding habits vary with age and are not well defined (opportunistic). Data for other biota (American Eel, Striped Bass, Channel/White Catfish, Weakfish, Osprey eggs) are presented in Appendix G.

The data show a decrease in fish tissue concentration from ~1970 to ~1990. However, over the past ~10 years, from 1990 to 2002 no decrease in concentration is evident. This is roughly consistent with the relatively constant sediment concentrations (Figure 5.7). The last two years show an increasing trend in fish tissue concentrations. This recent increase is seen in the White/Channel Catfish data as well (Appendix G). The model sediment concentrations for the Air Trend are at the high end of the data. If any biomagnification is accounted for the agreement worsens. The sediment concentrations for the Hudson Trend are at the low end of the data, which is more consistent when biomagnification is assumed to occur. Neither trend captures the constant concentration over the past ~10 years or increase over the last two years. This is an important discrepancy between the model and historical data. This could be the result of error(s) in the model, forcing functions and/or data.

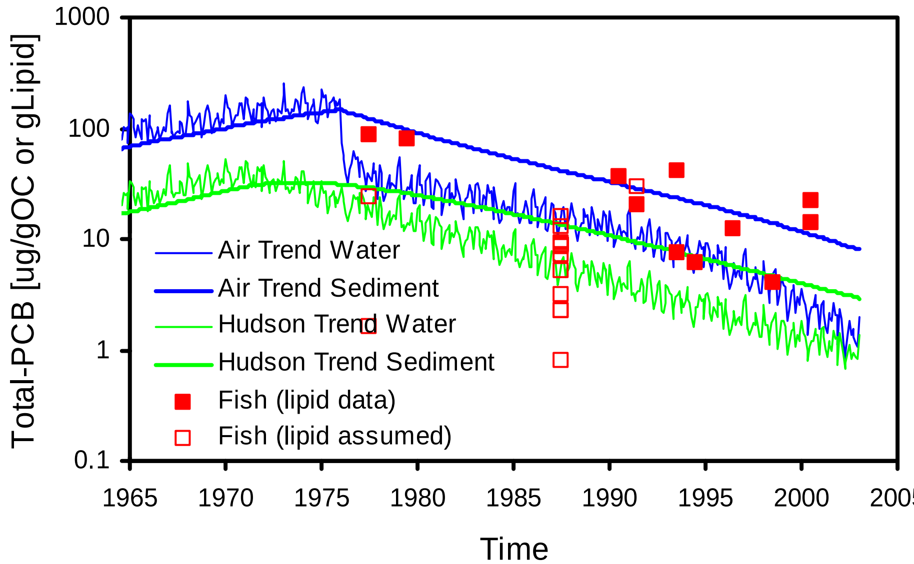


Figure 5.8(a) – Historical fish total-PCB concentration in Zone 2. Data are for White Perch. Model sediment results are for layer 1

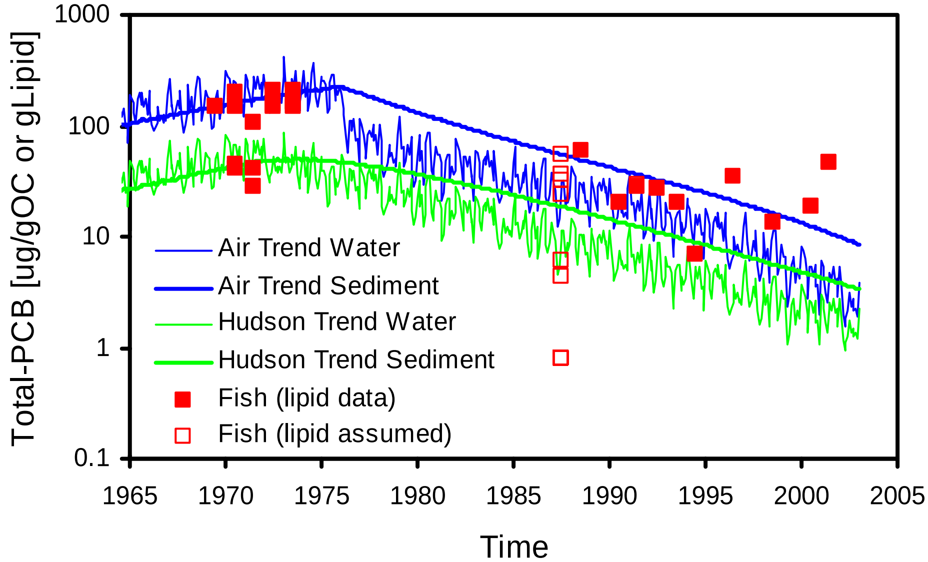


Figure 5.8(b) – Historical fish total-PCB concentration in Zone 3. Data are for White Perch. Model sediment results are for layer 1

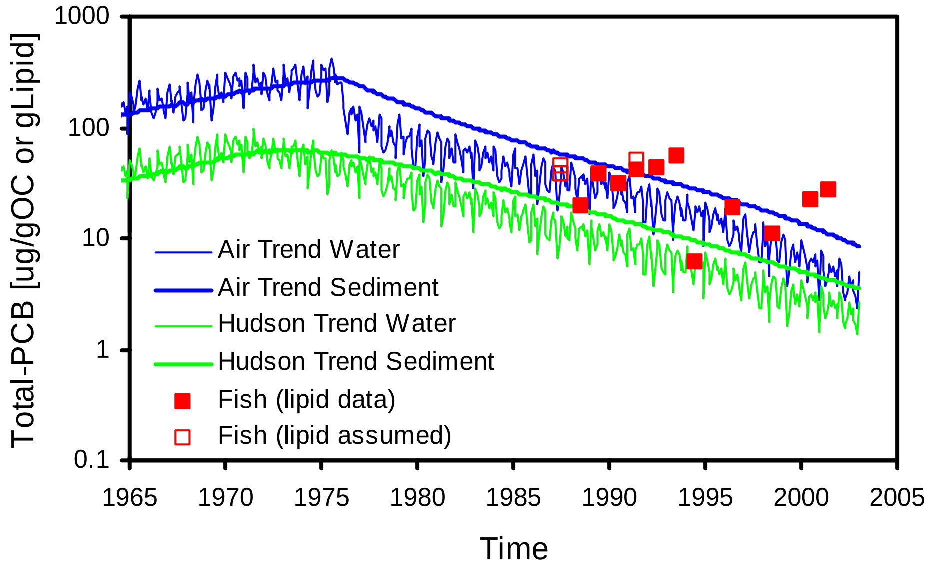


Figure 5.8(c) – Historical fish total-PCB concentration in Zone 4. Data are for White Perch. Model sediment results are for layer 1

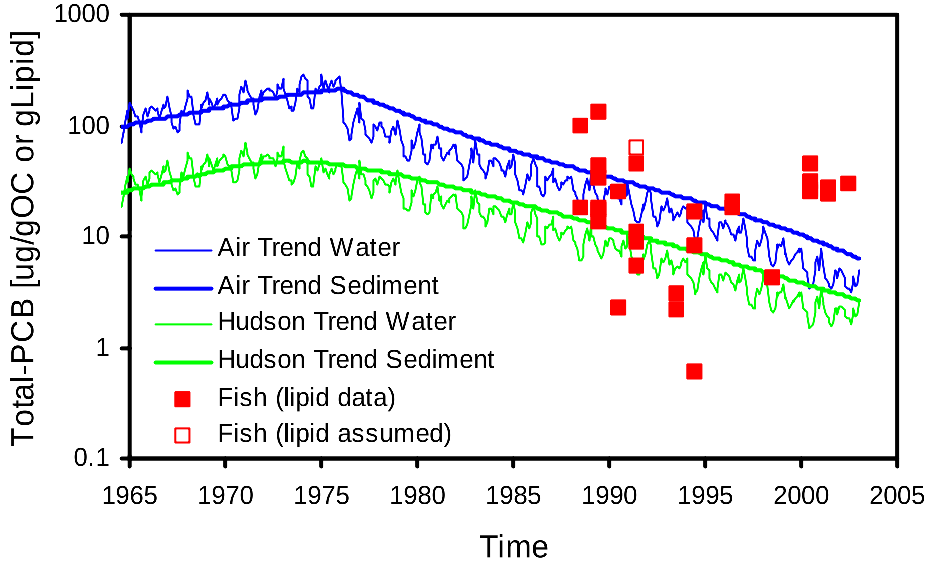


Figure 5.8(d) – Historical fish total-PCB concentration in Zone 5. Data are for White Perch. Model sediment results are for layer 1

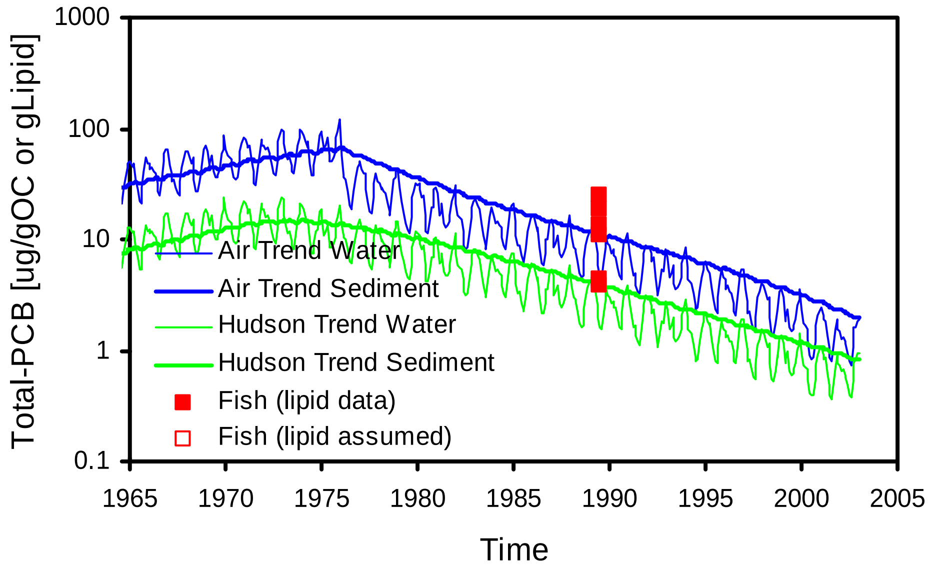


Figure 5.8(e) – Historical fish total-PCB concentration in Zone 6. Data are for White Perch. Model sediment results are for layer 1

5.4.4 Contemporary sediment data

A stringent test of the model is its ability to predict the presently observed PCB concentrations, using the historical loading. Contemporary sediment data are presented in Figure 5.9. The data were processed by DRBC by averaging the dry-weight PCB concentrations (μg/kg) by zone. However, sediment bed fraction organic carbon (foc) data were not averaged and therefore the organic carbon-based PCB concentrations (μg/gOC) vary somewhat within each zone.

The model-simulated concentrations for the two loading trends bracket the data in the upstream portion of the estuary (Zones 2 and 3). Below that the agreement is worse with the model progressively overpredicting concentrations with distance downstream. At the downstream end (Delaware Bay, Zone 6) the model overpredicts PCB concentrations for both loading trends by almost an order of magnitude. This is consistent with the model-data comparison for historical sediment concentrations presented in Section 5.4.2. Although the model is within the range of the historic sediment data (which has ~2-order of magnitude variability) at the end of the simulation period, it clearly tends to overpredict the observed sediment concentrations. This could be related to the inability of the model to simulate the estuarine turbidity maximum and associated effect on PCB fate and transport. On the other hand, a unit load simulation (results not presented here) demonstrated that the PCB mass in that part of the estuary is predominantly from the Atlantic Ocean. It is possible that the loading trends are not applicable to the Atlantic Ocean concentration. Due to the large volume the Atlantic Ocean responds slowly to changes in input. It is expected that applying the loading trend to the Atlantic Ocean resulted in an overestimation of the historical boundary concentration. The inability of the model to reproduce the data is therefore not necessarily a shortcoming of the model, but could be a shortcoming of the method used to develop the historical ocean boundary condition.

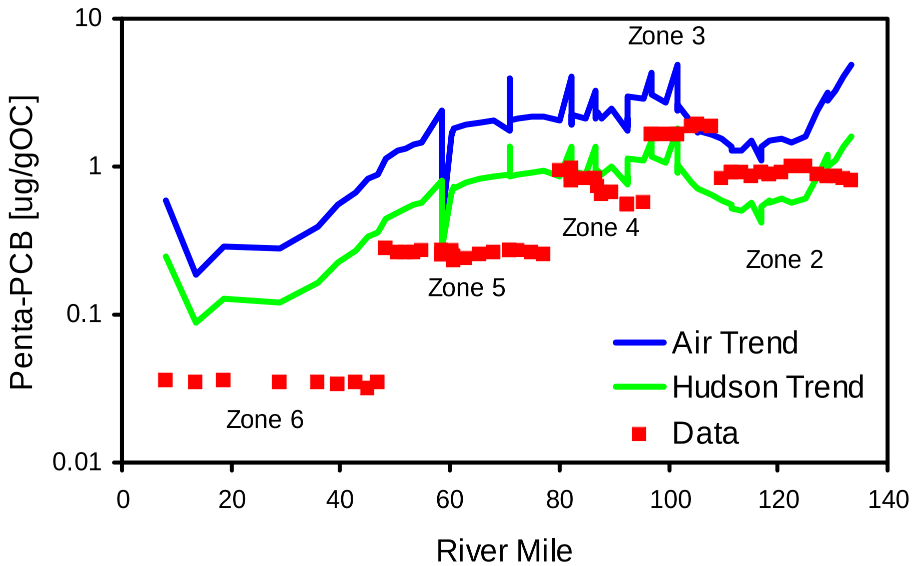


Figure 5.9 – Contemporary surface sediment penta-PCB concentrations. Model results are for sediment layer 1

5.4.5 Dated core data

The concentrations from the dated core are presented in Figure 5.10. Measured sediment concentrations on an organic carbon basis are compared to modeled water column concentrations on a particulate organic carbon basis. At first glance it might seem more appropriate to compare the data to sediment concentrations, but that would not be correct. That is because the sediment bed simulated by the model corresponds to the bioturbated sediments present throughout most of the estuary. However, the dated sediment core was collected from a location where there was apparently no significant bioturbation. The concentrations in the dated core are a record of the PCB concentration of depositing solids, and therefore the data are compared to PCB concentrations on organic carbon in the water column corresponding to the time of deposition.

The data show a relatively rapid increase in concentrations over the period 1950-60, followed by a smooth peak (1960-1980) and then decreasing concentrations from 1980 to the present. Neither loading trend predicts the rapid increase from 1950-1960. It is possible that this is a result of an error in the loading trend, model or data. To answer that question addition sediment cores should be examined. Post 1960 the Air Trend is in good agreement with the data (besides overpredicting the peak in 1970). The Hudson Trend clearly underpredicts concentrations after 1960.

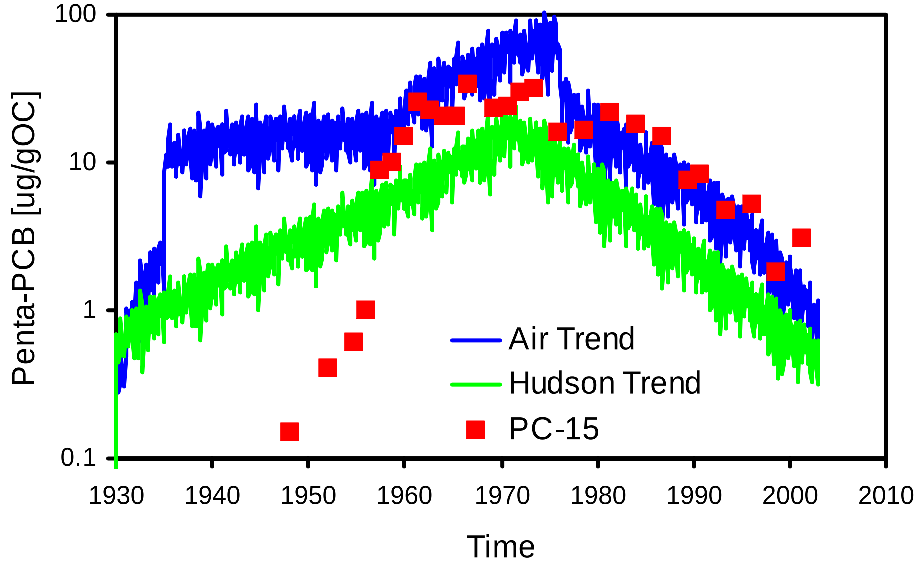


Figure 5.10 – Historical water column penta-PCB concentrations. Data are from Woodbury Creek core (PC-15; Sommerfield and Madsen, 2003; Eisenreich, 2003)

Depth was converted to time using 1.5 cm/yr net deposition rate. Model results are for Segment 44.

5.5 Conclusions and Recommendations

5.5.1 General conclusions

Historical hindcast simulations (1930-2002) were performed to check the long-term (decadal scale) behavior of the model. There are large uncertainties in the PCB forcing functions (current loads, historical loading trend) and ambient concentration data. Also, the present analysis neglects episodic events (e.g. hurricanes, 50-year flood) and long-term changes in non-PCB forcing functions (e.g. POC loads from municipal wastewater treatment plants, non-point sources) that could be important in the fate and transport of PCBs on the decadal scale. Therefore a meaningful quantitative statistical model-data comparison can not be performed and only a qualitative appraisal is made.

Based on our review of the hindcast simulation results with the current model: (1) The model is in reasonable agreement with the historical water column concentrations, both observed and deduced from the dated core for the period following the 1980s; (2) The model is in reasonable agreement with the contemporary sediment data in the upper estuary (Zones 2-3); (3) The model appears to be inconsistent with the historical sediment data. The model predicts a relatively fast rate of decrease in sediment concentrations which is not seen in the data, although that comparison is limited by the high variability in the sediment data; (4) The model predicted time course of water column and sediment bed concentrations also appear to be inconsistent with the fish tissue concentrations. The PCB concentrations in the fish have remained relatively constant over the past 10 years and increased over the past 2 years, which is not reproduced by the model. Thus there appears to be an important inconsistency between the historical sediment and fish tissue data and the model predictions. At present it is not clear what the source(s) of the problem is. Possible causes include error(s) in (1) forcing functions (current and/or historical), (2) the model (e.g. mixed layer depth) and/or (3) the data or how they are interpreted.

Recommendations are presented for model improvements in three areas: (1) PCB forcing functions, (2) the effect of episodic events and long-term changes in non-PCB forcing functions, and (3) sediments, bioaccumulation and fish tissue concentrations. It is important to resolve these discrepancies for the next phase of the TMDL process.

5.5.2 PCB Forcing Functions

Background

There are large uncertainties in the PCB forcing functions for the major source categories, especially the Contaminated Sites, non-point sources and possibly the gas phase source. These large uncertainties are the result of limitations in field sampling and analytical programs (number of samples, spatial and temporal resolution) and data analysis techniques (how these measurement are used to compute annual loading sequences). The uncertainty in the current forcing functions translates directly into uncertainties in the historical forcing functions, because a back-scaling methodology is used to derive the historical loadings. This limits the accuracy of the hindcast simulation.

The uncertainty in forcing functions also affects the model calibration. Suppose the Contaminated Sites loadings were underestimated. Then the model would be predicting lower water column PCBs than are actually measured. The only possible source would be the sediment, assuming all other sources are known. Therefore the sediment-water exchange would need to be increased. Conversely if the loading were overestimated, then removal processes (i.e. burial) would need to be increased. Therefore, the uncertainty in PCB forcing functions is directly relevant to assimilative capacity of the estuary and the TMDL calculation.

Understanding current loadings is also important for management. Targeting what might turn out to be minor sources will be costly and fail to achieve the desired reduction in PCB concentrations. It is necessary to properly identify and quantify the sources of PCBs in order to develop appropriate measures to address those sources.

Suggested tasks

It is recommended to reduce the uncertainty in the following loading categories:

- *Contaminated Sites.* It is possible that the mass flux from the Contaminated Sites varies over a wide range and that a small number of sites contribute a large fraction of the loadings. Those sites should be identified based on the current information. Then additional data collection and load estimation should be performed using site-specific analysis. Differences in transport pathways (e.g. rainfall runoff, groundwater migration) should be taken into account.
- *Atmospheric Loading & Boundary.* The model predicts that gas transfer of PCBs across the atmosphere-water interface is an important process. Depending on the concentration gradient across this surface, which varies in space, time and scenario (i.e. TMDL condition), the atmosphere can be a significant source or sink of PCBs to/from the estuary. It is expected that the temporal and spatial variability in the atmospheric gas-phase concentration is large. Additional data collection should be performed to characterize the gas phase concentration. The use of global models (i.e. Globo-POP, Wania and Daly, 2002) to predict the historic atmospheric gas phase concentration should be investigated. Also, cores from areas that are not hydrologically connected to the estuary and do not receive any significant non-atmospheric load of PCBs (i.e. pristine areas) should be collected, since they would record atmospheric loading. This is particularly important in the Camden region since a large present day source appears to be active. It would be important to know if this source was present in the past.
- *Unidentified historical deposits.* It is possible that historical deposits of PCBs are contributing to the present concentrations, but have not yet been identified. Shoaling areas and marsh sources may also be important. Additional sediment sampling in these locations should be performed.
- *Tributaries.* Loadings from tributaries should be calculated using standard regression techniques (rating curves) applied to flow, organic carbon and PCBs. This will require additional data collection to define the relationship between these parameters. Sediment cores should be collected upstream of the head of tides to determine the historical loadings from tributaries.
- *Tidewater.* Present estimates of PCB loadings from the "tidewater" area (direct ungaged runoff) are based on literature values. Site specific data should be collected and analyzed to confirm those estimates are representative of the Delaware Estuary area.
- *Atlantic Ocean.* The historical time trend of PCB concentrations in the Atlantic Ocean should be refined by collecting sediment cores on the shelf. Also, the use of global models (i.e. Globo-POP, Wania and Daly, 2002) to define the historical concentration should be investigated.
- *Historical time trend.* The shape and uncertainty of the historical loading time trend and the applicability to each loading category (e.g. Atlantic Ocean boundary) should be investigated. For significant individual sources (e.g. Contaminated Sites) this analysis should be done on a site-specific basis.

Alternate methods for extending the Breivik et al. estimate from 2000 to 2002 and the Thomann/Farley estimate from 1994 to 2002 should be investigated.

5.5.3 Effect of Episodic events and long-term changes in non-PCB forcing functions

Background

The current version of the model is based on a simulation period with forcing functions representative of average conditions. The hindcast simulation was performed by cycling a 1-year period representative of average conditions. However, the transport of solids and therefore organic carbon and associated PCBs is highly event driven. On a long-term average, episodic events (e.g. hurricanes, 50-year flood) could constitute a significant import and/or export of PCBs from the estuary. Also, it is expected that the organic carbon input from point (municipal wastewater treatment plants) and non-point (erosion control practices) sources has changed significantly over the hindcast simulation period. The effects of changes in organic carbon input can be relatively direct (e.g. more POC → more POC settling → more PCBs settling) or more indirect (e.g. more DOC → less dissolved oxygen → less bioturbation → less sediment bed PCB flux).

Suggested tasks

- The effect of episodic events should be investigated by estimating the response of the forcing functions (i.e. tributary loadings) and model transport processes (e.g. sediment resuspension) to such events.
- The sensitivity of the hindcast simulation to changes in historical organic carbon discharges from municipal wastewater treatment plants and non-point sources should be investigated.

5.5.4 Sediments, bioaccumulation & fish tissue concentrations

Background

The model predicts a decline in the water column and sediments in the last ten years that has not been observed in sediment and fish tissue concentration data. This points to an important problem in the model and/or PCB forcing functions. This is an important issue, because reducing PCB concentrations in fish tissue is the ultimate goal of the overall TMDL process. If the model can not be used to predict the response of the fish tissue concentration under various management alternatives its utility is severely limited.

Suggested tasks

- A careful analysis of the fish tissue data should be performed. Differences in sampling (e.g. time of year, size of fish) and data analysis techniques (e.g. how non-detects are handled) can introduce biases, which could be responsible for the recent increase seen in the fish tissue data.
- A similar analysis should be performed for the historical surface sediment data. For sediment data, spatial variability (e.g. channel vs. bank) can introduce biases into the database.
- Additional sediment cores should be collected in order to validate the temporal trend seen in the Woodbury core
- A food chain bioaccumulation model for the Delaware Estuary should be developed. The model should be time variable, account for all major trophic levels (e.g. benthic invertebrates, small fish, large fish), various age classes and migratory behavior (if applicable). The model should be coupled to the present Delaware Estuary PCB fate and transport model and should include both water column and sediment food chains.

6 Conclusions

The overall objective of the model calibration was to accurately represent the principal environmental processes influencing the transport and fate of penta-PCBs in the Delaware River and Estuary. These processes include hydrodynamics, sorbent (organic carbon) dynamics and partitioning of PCBs to organic carbon in the water column and bedded sediments. This model was calibrated to ambient data for biotic carbon (BIC) and particulate detrital carbon (PDC) in the water column, and to available data for net solids burial in the sediments. Finally, the calibrated sorbent dynamics model was used to drive a mass balance model of penta-PCBs in the water column and sediments.

Daily loads of organic carbon and penta-PCB were estimated for each day of the 577 day continuous simulation period spanning September 1, 2001 through March 31, 2003 for relevant source categories, including contaminated sites, non-point sources, point discharges, model boundaries, tributaries, atmospheric deposition; and CSOs.

In order to assess the uncertainty associated with the load estimation calculations, a Monte Carlo analysis was performed for each of the PCB source categories. This analysis allowed estimation of the uncertainty for each source category, comparisons of uncertainty between categories, and identification of reasonable upper and lower limits for loadings for each category and for the overall penta-PCB load. Scaled loads corresponding to the 20th and 80th percentile of the overall penta-PCB loading range yielded water column concentrations within -10% to +20% of the unscaled loads.

Ambient water samples were collected from the mainstem Delaware Estuary for the analysis of particulate and dissolved PCBs, total suspended solids, dissolved organic carbon (DOC), chlorophyll a, and particulate organic carbon (POC). Twenty four main stem channel sites were sampled under a range of flows. The data collected allowed initial quantitation of dissolved and particulate PCB levels as well as organic carbon in the mainstem Delaware Estuary. The resultant monitoring data were used as calibration targets for the model.

DRBC and LTI enhanced EPA's Water Quality Simulation Program (WASP) Version 5.12 to develop a general purpose sorbent dynamic PCB model for the Delaware River Estuary. The model simulates tidal flows, and spatial and temporal distributions of OC and penta-PCB. Comparisons of simulated to measured water quality concentrations indicate generally good agreement and low bias of the estimate for organic carbon and penta-PCB. The correlation coefficients for particulate and dissolved penta-PCB exceed EPA's recommended correlation coefficient acceptance criteria for water quality variables.

Historical hindcast simulations (1930-2002) were performed to check the long-term (decadal scale) behavior of the model. A review of the hindcast simulation results using the current model showed: (1) The model is in reasonable agreement with the historical water column concentrations, both observed and deduced from the dated core for the period following the 1980s; (2) The model is in reasonable agreement with the contemporary sediment data in the upper estuary (Zones 2-3); (3) The model appears to be inconsistent with the historical sediment data; (4) The model predicted time course of water column and sediment bed concentrations also appear to be inconsistent with the fish tissue concentrations. At present it is not clear what the source(s) of the two inconsistencies (sediment and fish tissue) is (are). Possible causes include error(s) in (1) forcing functions (current and/or historical), (2) the model (e.g. mixed layer depth) and/or (3) the data or how they are interpreted.

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